Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photocatalyst-Free Decarboxylative Aminoalkylation of Imidazo[1,2-*a*]pyridines with *N*-Aryl Glycines Enabled by Visible Light

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Supporting Information

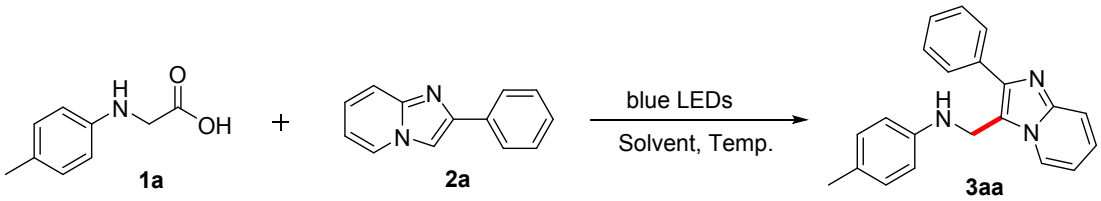
Contents:

1. General Information

Unless otherwise indicated, all reagents were purchased from commercial distributors and used without further purification. ^{1}H NMR and ^{13}C NMR were recorded at 400 MHz, 500 MHz and 100 MHz, 125 MHz respectively, using tetramethylsilane as an internal reference. High-resolution mass spectra (HRMS) were measured on a quadrupole time-of-flight (Q-TOF) mass spectrometer instrument with an electrospray ionization (ESI) source. Melting points were uncorrected. Flash column chromatography was performed over silica gel 200-300 mesh. Thin-layer chromatography (TLC) was carried out with silica gel GF254 plates. *N*-aryl glycines **1** and imidazo[1,2-*a*]pyridines **2** were prepared according to the previous reported protocols.[1,2]

2. Optimization of the Reaction Conditions

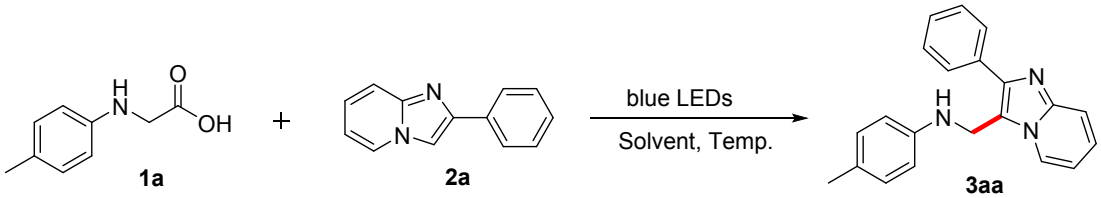
Table S1. Screening of Catalysts and Oxidants[a]



Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]
1	$Ru(bpy_3)Cl_2 \cdot 6H_2O$	air	MeCN	62
2	$Ir(bpy)_3$	air	MeCN	21
3	Eosin B	air	MeCN	44
4	Eosin Y	air	MeCN	52
5	Acr^{+}-Mes-ClO_4^{-}	air	MeCN	60
6		air	MeCN	69
7		TBHP	MeCN	71
8		DTBP	MeCN	70
9		TBPB	MeCN	67
10		DCP	MeCN	69
11		BPO	MeCN	43
12		$K_2S_2O_8$	MeCN	15
13		O_2	MeCN	58

(a) Reaction conditions: **1a** (0.26 mmol), **2a** (0.2 mmol), catalyst (2 mol %), air or oxidant (2 equiv), solvent (2 mL) at room temperature under irradiation of 18 W blue LED light for 16-35 hrs. (b) Isolated yield based on **2a**.

Table S2. Screening of Solvents, Substrate ratio, *etc.*[a]



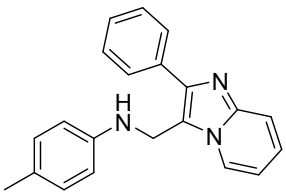
1a 2a 3aa

Entry	Catalyst	Oxidant	Solvent	Yield(%)[b]
1		air	DCE	72
2		air	DCM	30
3		air	EtOH	66
4		air	EtOAc	50
5		air	Acetone	46
6		air	DMSO	trace
7[c]		air	DMF	N.P.
8		air	Toluene	75
9[d]		**air**	**Toluene**	**82**
10[e]		air	Toluene	73
11[d,f]		air	Toluene	trace

(a) Reaction conditions: **1a** (0.26 mmol), **2a** (0.2 mmol), solvent (2 mL) at room temperature under irradiation of 18 W blue LED light for 16-35 hrs. (b) Isolated yield based on **2a**. (c) N.P. = No product. (d) **1a** (0.3 mmol). (e) **1a** (0.4 mmol). (f) The reaction was performed in darkness or without additional irradiation of blue LED light.

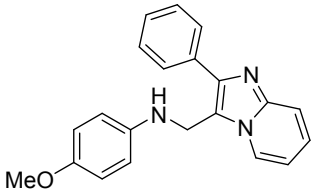
3. Characterization Data

4-Methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3aa)



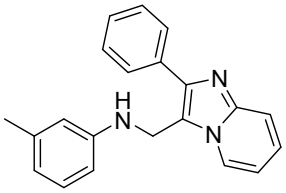
Light yellow solid; mp 164.1-165.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, J = 5.6 Hz, 1H), 7.80 (d, J = 5.6 Hz, 2H), 7.73 (d, J = 7.2 Hz, 1H), 7.46 (t, J = 6.0 Hz, 2H), 7.38 (t, J = 6.0 Hz, 1H), 7.28 (t, J = 6.2 Hz, 1H), 7.08 (t, J = 6.4 Hz, 2H), 6.87 (t, J = 5.4 Hz, 1H), 6.69 (d, J = 6.8 Hz, 2H), 4.70 (s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.2, 144.6, 133.9, 130.0, 128.8, 128.4, 128.1, 127.8, 125.0, 124.2, 117.6, 116.7, 113.3, 112.5, 38.6, 20.5; HRMS (ESI) calcd for $C_{21}H_{20}N_3$ $(M+H)^+$ 314.1652, found 314.1661.

4-Methoxy-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ba)



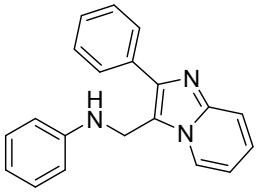
Light yellow solid; mp 173.4-174.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J = 7.0 Hz, 1H), 7.80-7.73 (m, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.25-7.20 (m, 1H), 6.91-6.77 (m, 3H), 6.74-6.66 (m, 2H), 4.64 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$): δ 152.8, 145.2, 144.5, 141.8, 134.0, 128.8, 128.4, 128.0, 125.0, 124.3, 117.5, 116.8, 115.0, 114.5, 112.5, 55.5, 39.2; HRMS (ESI) calcd for $C_{21}H_{18}N_3O$ $(M-H)^-$ 328.1455, found 328.1452.

3-Methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ca)



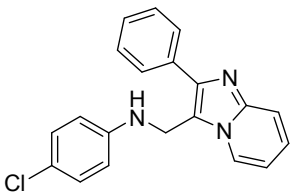
Brown solid; yield: mp 148.0-149.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 6.8 Hz, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 8.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.18-7.08 (m, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.71 (t, J = 6.6 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.48 (s, 2H), 3.73 (brs, 1H), 4.57 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 145.2, 144.6, 139.4, 133.9, 129.4, 128.8, 128.4, 128.0, 124.9, 124.1, 119.3, 117.5, 116.6, 113.9, 112.5, 110.4, 38.2, 21.6; HRMS (ESI) calcd for $C_{21}H_{20}N_3$ $(M+H)^+$ 314.1652, found 314.1649.

***N*-((2-Phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3da)**



Light yellow solid; mp 123.5-124.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 5.2 Hz, 1H), 7.78 (d, J = 5.2 Hz, 2H), 7.67 (d, J =7.2 Hz, 1H), 7.44 (d, J = 6.0 Hz, 2H), 7.36 (d, J = 6.0 Hz, 1H),7.28-7.22 (m, 3H), 6.83 (m, 2H), 6.75 (d, J = 6.0 Hz, 2H), 4.69 (d, J = 2.0 Hz, 2H), 3.85 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 145.2, 144.7, 133.9, 129.5, 128.8, 128.4, 128.1, 125.0, 124.1, 118.4, 117.6, 116.4, 113.2, 112.6, 38.3; HRMS (ESI) calcd for $C_{20}H_{18}N_3$ $(M+H)^+$ 300.1495, found 300.1494.

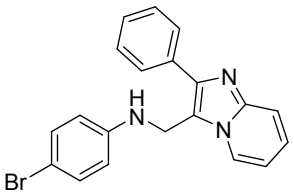
4-Chloro-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ea)



Light yellow solid; mp 194.5-195.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 5.6 Hz, 1H), 7.74 (d, J = 6.0 Hz, 2H), 7.67 (d, J =7.2 Hz, 1H), 7.44 (d, J = 6.0 Hz, 2H), 7.37 (d, J = 6.0 Hz, 1H), 7.25 (t, J = 6.0 Hz, 1H), 7.20

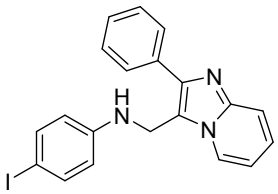
(d, J = 6.8 Hz, 2H), 6.85 (t, J = 5.4 Hz, 1H), 6.66 (d, J = 7.2 Hz, 2H), 4.65 (s, 2H), 3.91 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 145.3, 144.8, 133.8, 129.3, 128.8, 128.4, 128.2, 125.1, 124.0, 123.1, 117.6, 116.1, 114.2, 112.7, 38.4; HRMS (ESI) calcd for $C_{20}H_{17}ClN_3$ $(M+H)^+$ 334.1106, found 334.1106.

4-Bromo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3fa)



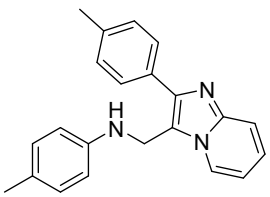
Light yellow solid; mp 129.0-130.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 6.8 Hz, 1H), 7.75 (d, J = 7.2 Hz, 2H), 7.68 (d, J = 9.2 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.38 (d, J = 7.6 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 7.27-7.17 (m, 1H), 6.85 (t, J = 6.8 Hz, 1H), 6.62 (d, J = 8.8 Hz, 2H), 4.66 (s, 2H), 3.88 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 145.3, 144.9, 133.8, 132.2, 128.8, 128.4, 128.2, 125.0, 123.9, 117.7, 116.0, 114.7, 112.7, 110.2, 38.3; HRMS (ESI) calcd for $C_{20}H_{16}BrN_3$ $(M+H^+)$ 378.0600, found 378.0599.

4-Iodo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ga)



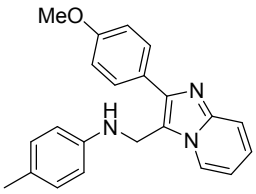
Light yellow solid; mp 187.3-188.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10 (d, J = 7.0 Hz, 1H), 7.79-7.69 (m, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.24 (t, J = 8.5 Hz 1H), 6.96 (t, J = 8.8 Hz, 2H), 6.83 (t, J =7.0 Hz, 1H), 6.67 (dd, J =9.0, 4.5 Hz, 2H), 4.63 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 144.7, 143.9, 133.9, 128.8, 128.4, 128.1, 125.1, 124.1, 117.6, 116.4, 116.0, 115.8, 114.1, 114.0, 112.6, 38.9; HRMS (ESI) calcd for C20H16IN3 $(M+H)^+$ 470.0360, found 470.0342.

4-Methyl-*N*-((2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ab)



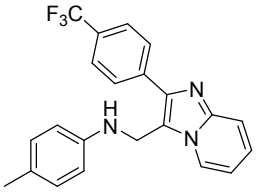
Light yellow solid; mp 151.4-152.6 °C; 1H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, J = 6.8 Hz, 1H), 7.65 (d, J = 7.9 Hz, 3H), 7.27-7.17 (m, 3H), 7.06 (d, J = 8.2 Hz, 2H), 6.78 (t, J = 6.7 Hz, 1H), 6.67 (d, J = 8.3 Hz, 2H), 4.63 (s, 2H), 3.75 (brs, 1H), 2.37 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 145.1, 144.5, 137.9, 131.0, 130.0, 129.5, 128.2, 127.6, 124.9, 124.1, 117.4, 116.4, 113.2, 112.4, 38.6, 21.3, 20.5; HRMS (ESI) calcd for $C_{22}H_{22}N_3$ $(M+H)^+$ 328.1808, found 328.1802.

***N*-((2-(4-Methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3ac)**



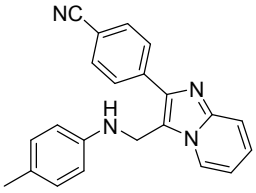
Light yellow solid; mp 174.3-175.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 5.6 Hz, 1H), 7.71 (dd, J = 5.6 Hz, J = 1.6 Hz, 2H), 7.65 (d, J = 7.2 Hz, 1H), 7.24-7.20 (m, 1H), 7.07 (d, J = 6.4 Hz, 2H), 6.96 (dt, J = 7.2 Hz, J = 1.8 Hz, 2H), 6.81 (td, J = 5.4 Hz, J = 0.8 Hz, 1H), 6.68 (d, J = 6.4 Hz, 2H), 4.64 (s, 2H), 3.83 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 145.4, 145.1, 144.4, 130.0, 129.6, 127.7, 126.5, 124.8, 124.0, 117.3, 116.0, 114.2, 113.3, 112.4, 55.3, 38.6, 20.5; HRMS (ESI) calcd for $C_{22}H_{22}N_3O$ $(M+H)^+$ 344.1757, found 344.1763.

4-Methyl-*N*-((2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ad)



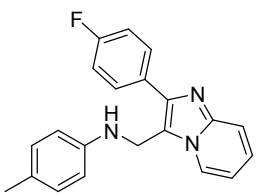
Light yellow solid; mp 149.6-150.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 5.2 Hz, 1H), 7.82 (d, J = 6.4 Hz, 2H), 7.61 (d, J = 6.8 Hz, 3H), 7.21 (t, J = 6.2 Hz, 1H), 7.09 (d, J = 6.4 Hz, 2H), 6.77 (t, J = 5.4 Hz, 1H), 6.71 (d, J = 6.0 Hz, 2H), 4.59 (s, 2H), 4.03 (brs, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.2, 142.7, 137.4, 130.0, 129.7 (q, J = 25.7 Hz), 128.3, 127.8, 125.6 (q, J = 2.9 Hz), 125.4, 124.3 (q, J = 216.6 Hz), 124.2, 117.6, 117.5, 113.2, 112.8, 38.4, 20.5; HRMS (ESI) calcd for $C_{22}H_{19}F_3N_3$ $(M+H)^+$ 328.1526, found 328.1528.

Ethyl 2-(6,6-dimethyl-2,4-dioxo-3-azabicyclo[3.1.0]hexan-3-yl)-2-(*p*-tolylamino)acetate (3ae)



Light yellow solid; mp 168.4-168.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 5.6 Hz, 1H), 7.88 (d, J = 6.4 Hz, 2H), 7.69-7.65 (m, 3H), 7.28 (t, J = 6.4 Hz, 1H), 7.10 (d, J = 6.4 Hz, 2H), 6.86 (t, J = 5.4 Hz, 1H), 6.70 (d, J = 6.4 Hz, 2H), 4.64 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 145.0, 142.3, 138.5, 132.5, 130.1, 128.6, 128.1, 125.7, 124.2, 118.9, 117.9, 117.8, 113.3, 113.1, 111.3, 38.5, 20.5; HRMS (ESI) calcd for $C_{22}H_{17}N_4$ $(M-H)^-$ 337.1459, found 337.1456

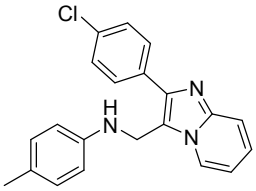
***N*-((2-(4-Fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3af)**



Light yellow solid; mp 178.1-179.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, J = 6.8 Hz, 1H), 7.71-7.61 (m, 2H), 7.56 (d, J = 9.2Hz, 1H), 7.21-7.08 (m,

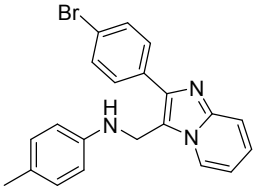
1H), 7.07-6.91 (m, 4H), 6.73 (t, J = 6.4 Hz, 1H), 6.60 (d, J = 8.4 Hz, 2H), 4.54 (s, 2H), 3.70 (brs, 1H), 2.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7 (d, J = 246.0 Hz) , 145.2, 145.1, 143.7, 130.1, 130.0, 127.9, 125.1, 124.1, 117.5, 116.5, 115.8 (d, J = 21.5 Hz), 113.3, 112.6, 38.5, 20.5; HRMS (ESI) calcd for $C_{21}H_{18}FN_3$ $(M-H)^-$ 330.1412, found 330.1412.

_N_-((2-(4-Chlorophenyl)imidazo[1,2-_a_]pyridin-3-yl)methyl)-4-methylaniline (3ag)



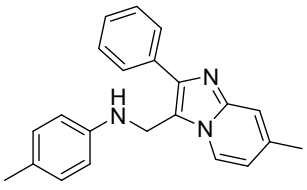
Light yellow solid; mp 128.5-128.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, J = 7.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 9.0 Hz, 1H), 7.34 (d, J = 7.0 Hz, 2H), 7.23-7.17 (m, 1H), 7.08 (d, J = 8.5 Hz, 2H), 6.79 (t, J = 6.8 Hz, 1H), 6.69 (d, J = 8.5 Hz, 2H), 4.58 (s, 2H), 3.90 (brs, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.1, 143.2, 133.9, 132.3, 130.0, 129.4, 128.9, 127.7, 125.2, 124.1, 119.9, 119.2, 117.4, 116.8, 113.2, 112.6, 38.4, 20.5; HRMS (ESI) calcd for $C_{21}H_{19}ClN_3$ $(M+H)^+$ 348.1262, found 348.1262.

_N_-((2-(4-Bromophenyl)imidazo[1,2-_a_]pyridin-3-yl)methyl)-4-methylaniline (3ah)



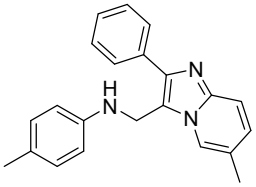
Light yellow solid; mp 181.1-182.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 5.6 Hz, 1H), 7.63-7.59 (m, 3H), 7.50 (dt, J = 6.8 Hz, J = 1.6 Hz, 2H), 7.23-7.20 (m, 1H), 7.08 (d, J = 6.4 Hz, 2H), 6.80 (td, J = 5.6 Hz, J = 1.0 Hz, 1H), 6.68 (d, J = 6.4 Hz, 2H), 4.58 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.1, 143.2, 132.8, 131.9, 130.0, 129.7, 127.8, 125.2, 124.1, 122.2, 117.5, 116.8, 113.3, 112.7, 38.5, 20.5; HRMS (ESI) calcd for $C_{21}H_{19}BrN_3$ $(M+H)^+$ 392.0757, found 392.0760.

4-Methyl-_N_-((7-methyl-2-phenylimidazo[1,2-_a_]pyridin-3-yl)methyl)aniline (3ai)



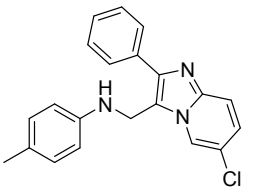
Light yellow solid; mp 174.0-175.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 5.2 Hz, 1H), 7.75 (d, J = 5.2 Hz, 2H), 7.43-7.40 (m, 3H), 7.35-7.32 (m, 1H), 7.07 (d, J = 6.4 Hz, 2H), 6.67 (d, J = 6.8 Hz, 2H), 6.62 (dd, J = 5.2 Hz, J = 1.2 Hz, 1H), 4.62 (s, 2H), 3.76 (brs, 1H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 145.4, 144.1, 136.0, 134.0, 130.0, 128.7, 128.3, 127.9, 127.6, 123.4, 116.1, 115.9, 115.1, 113.3, 38.6, 21.4, 20.5; HRMS (ESI) calcd for $C_{22}H_{22}N_3$ $(M+H)^+$ 328.1808, found 328.1800.

4-Methyl-*N*-((6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3aj)



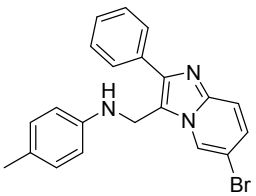
Light yellow solid; mp 195.8-196.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.75 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 9.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.09-7.05 (m, 3H), 6.70 (d, J = 8.0 Hz, 2H), 4.60 (s, 2H), 3.77 (brs, 1H), 2.30 (s,3H), 2.29(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5, 144.4, 144.3, 134.1, 130.0, 128.7, 128.2, 128.1, 127.9, 127.6, 122.2, 121.7, 116.8, 116.3, 113.3, 38.6, 20.5, 18.4; HRMS (ESI) calcd for $C_{13}H_{19}N_2O_3$ (M+H$^+$) 251.1390, found 251.1388.

***N*-((6-Chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3ak)**



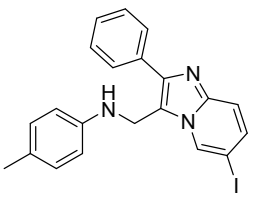
Light yellow solid; mp 144.6-145.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 1.2 Hz, 1H), 7.63-7.57 (m, 2H), 7.46 (d, J = 9.6 Hz, 1H), 7.33-7.24 (m, 3H), 7.06 (dd, J = 9.6, 2.0 Hz, 1H), 6.99 (d, J = 8.2 Hz, 2H), 6.61 (d, J = 8.4 Hz, 1H), 4.50 (s, 2H), 3.81 (brs, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 145.3, 143.5, 133.4, 130.0, 128.8, 128.3, 128.2, 128.0, 126.2, 122.2, 120.7, 117.8, 117.3, 113.5, 38.6, 20.4; HRMS (ESI) calcd for $C_{21}H_{18}ClN_3$ (M+H)$^+$ 348.1262, found 348.1260

***N*-((6-Bromo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3al)**



Light yellow solid; mp 157.3-158.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J = 1.6 Hz, J = 0.8 Hz, 1H), 7.70 (dt, J = 5.6 Hz, J = 1.2 Hz, 2H), 7.52 (dd, J = 7.2 Hz, J = 0.6 Hz, 1H), 7.41-7.38 (m, 2H), 7.36-7.33 (m, 1H), 7.25 (dd, J =7.6 Hz, J =1.6 Hz, 2H), 6.70 (dt, J = 7.6 Hz, J = 2.0 Hz, 1H), 6.69 (d, J = 6.8 Hz, 2H), 4.60 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 145.2, 143.6, 133.4, 130.0, 128.8, 128.4, 128.3, 128.1, 124.4, 118.1, 117.1, 113.5, 107.3, 38.6, 20.5; HRMS (ESI) calcd for $C_{21}H_{19}BrN_3$ (M+H)$^+$ 392.0757, found 392.0762.

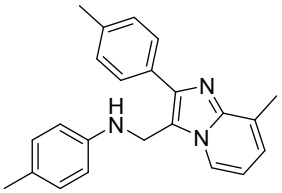
***N*-((6-Iodo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3am)**



Light yellow solid; mp 128.5-129.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.72-7.54 (m, 2H), 7.40-7.22 (m, 5H), 7.00 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 4.50 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2,

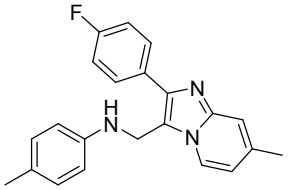
144.7, 143.6, 133.2, 133.1, 130.0, 129.2, 128.9, 128.4, 128.0, 118.4, 116.7, 113.5, 38.6, 20.5; HRMS (ESI) calcd for $C_{21}H_{17}IN_3$ $(M-H)^-$ 438.0473, found 438.0459.

4-Methyl-*N*-((8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3an)



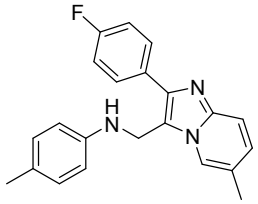
Light yellow solid; mp 189.4-191.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, J = 7.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 6.5 Hz, 1H), 6.73 (t, J = 7.0 Hz, 1H), 6.66 (d, J = 8.5 Hz, 2H), 4.63 (s, 2H), 2.67 (s, 3H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5, 145.4, 144.2, 137.7, 131.2, 129.9, 129.4, 128.4, 127.6, 127.4, 123.7, 121.9, 116.7, 113.2, 112.5, 38.7, 21.3, 20.5, 17.2; HRMS (ESI) calcd for $C_{23}H_{23}N_3$ $(M+H)^+$ 342.1965, found 342.1962.

***N*-((2-(4-Fluorophenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3ao)**



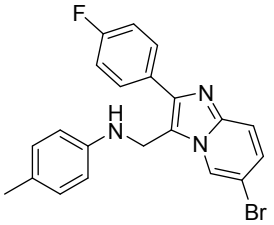
Light yellow solid; mp 163.7-165.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 7.0 Hz, 1H), 7.62-7.58 (m, 2H), 7.28 (s, 1H), 7.06-6.90 (m, 4H), 6.60 (d, J = 8.5 Hz, 2H), 6.53 (dd, J = 7.0, 1.5 Hz, 1H), 4.47 (s, 2H), 3.81 (brs, 1H), 2.31 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6 (d, J = 245.6 Hz), 145.5, 145.4, 143.1, 136.1, 130.1 (d, J = 3.1 Hz), 130.0, 129.9 (d, J = 8.2 Hz), 127.7, 123.3, 115.9, 115.8, 115.7 (d, J = 21.0 Hz), 115.2, 113.2, 38.5, 21.4, 20.5; HRMS (ESI) calcd for $C_{22}H_{20}FN_3$ $(M+H)^+$ 346.1714, found 346.1714.

***N*-((2-(4-Fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3ap)**



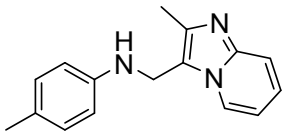
Light yellow solid; mp 170.0-173.7 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.69 (dd, J = 8.5, 5.5 Hz, 2H), 7.52 (d, J = 9.5 Hz, 1H), 7.07 (dd, J = 18.5, 8.5 Hz, 5H), 6.71 (d, J = 8.3 Hz, 2H), 4.55 (s, 2H), 3.88 (brs, 1H), 2.29 (d, J = 3.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6 (d, J = 245.6 Hz), 145.4, 144.1, 143.3, 130.1, 130.1 (d, J = 3.1 Hz), 129.8 (d, J = 8.0 Hz), 128.2, 127.7, 122.3, 121.6, 116.7, 116.1, 115.6 (d, J = 21.5 Hz), 113.2, 38.5, 20.5, 18.3; HRMS (ESI) calcd for $C_{22}H_{20}FN_3$ $(M-H)^-$ 344.1568, found 344.1564.

***N*-((6-Bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (3aq)**



Light yellow solid; mp 168.7-170.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.73-7.58 (m, 2H), 7.49 (d, J = 9.5 Hz, 1H), 7.28-7.24 (m, 1H), 7.13-6.99 (m, 4H), 6.72 (d, J = 8.5 Hz, 2H). 4.56 (s, 2H), 4.0 (brs, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8 (d, J = 246.1 Hz), 145.2, 144.2, 143.4, 130.0, 129.9 (d, J = 8.1 Hz), 129.4 (d, J = 3.2 Hz), 128.5, 128.1, 124.3, 117.9, 116.9, 115.8 (d, J = 21.4 Hz), 113.4, 107.4, 38.5, 20.5; HRMS (ESI) calcd for $C_{21}H_{17}BrFN_3$ $(M-H)^-$ 408.0517, found 408.0512.

4-Methyl-*N*-((2-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3ar)



Light yellow solid; mp 127.9-128.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 5.6 Hz, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.17 (dd, J = 6.4 Hz, J = 0.8 Hz, 3H), 7.06 (d, J = 6.8 Hz, 2H), 6.76 (t, J = 5.4 Hz, 1H), 6.67 (d, J = 5.4 Hz, 2H), 4.51 (s, 2H), 2.46 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 144.8, 141.4, 129.9, 127.7, 124.4, 124.1, 116.8, 116.7, 113.4, 112.0, 38.0, 20.5, 13.3; HRMS (ESI) calcd for $C_{16}H_{18}N_3$ $(M+H)^+$ 252.1495, found 252.1490.

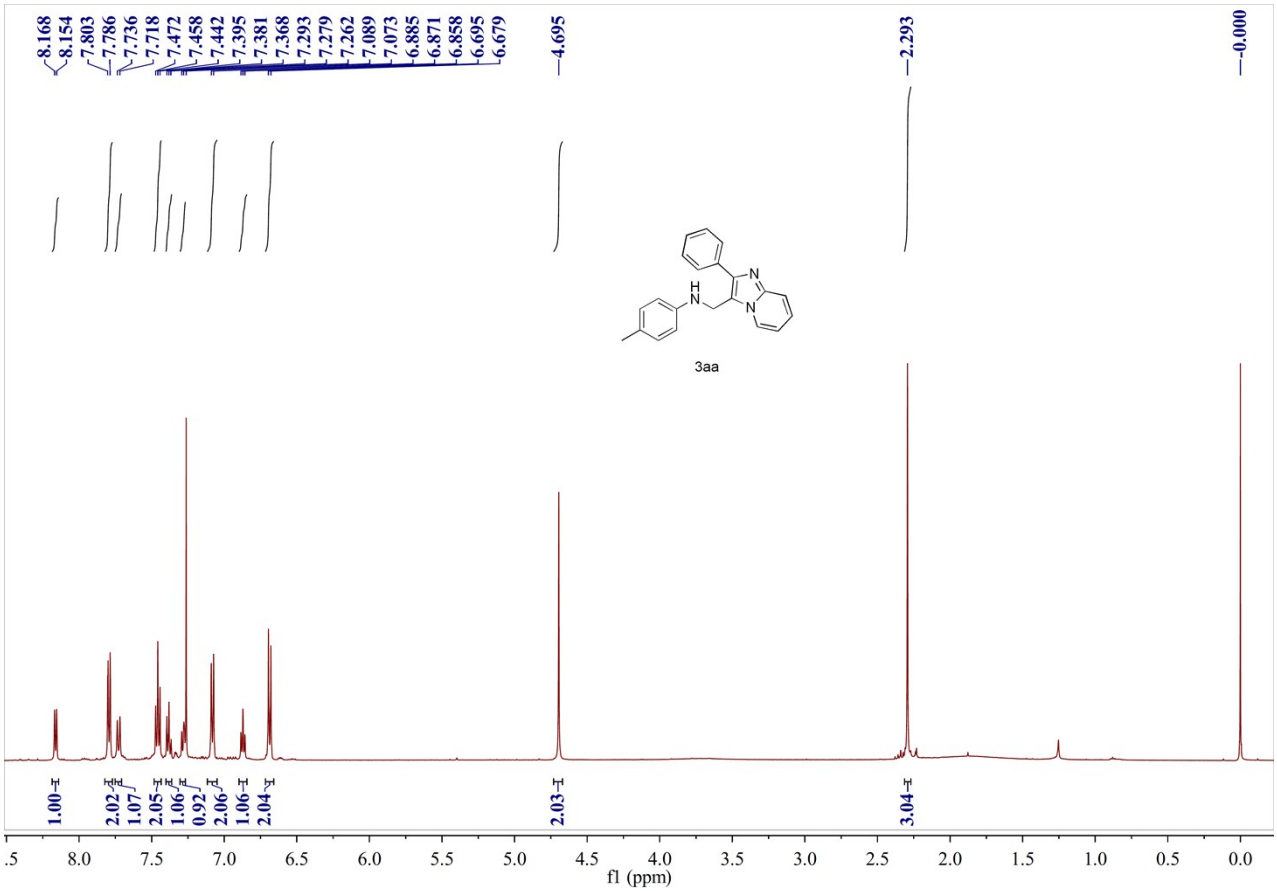
4. References

[1] (a) Y. Yin, Y. Dai, H. Jia, J. Li, L. Bu, B. Qiao, X. Zhao, Z. Jiang, *J. Am. Chem. Soc.,* 2018, **140**, 6083; (b) Z. Lu, R. J. Twieg, *Tetrahedron Lett.,* 2005, **46,** 2997; (c) W. K. Anderson, D. Bhattacharjee and D. M. Houston, *J. Med. Chem.,* 1989, **32**, 119.

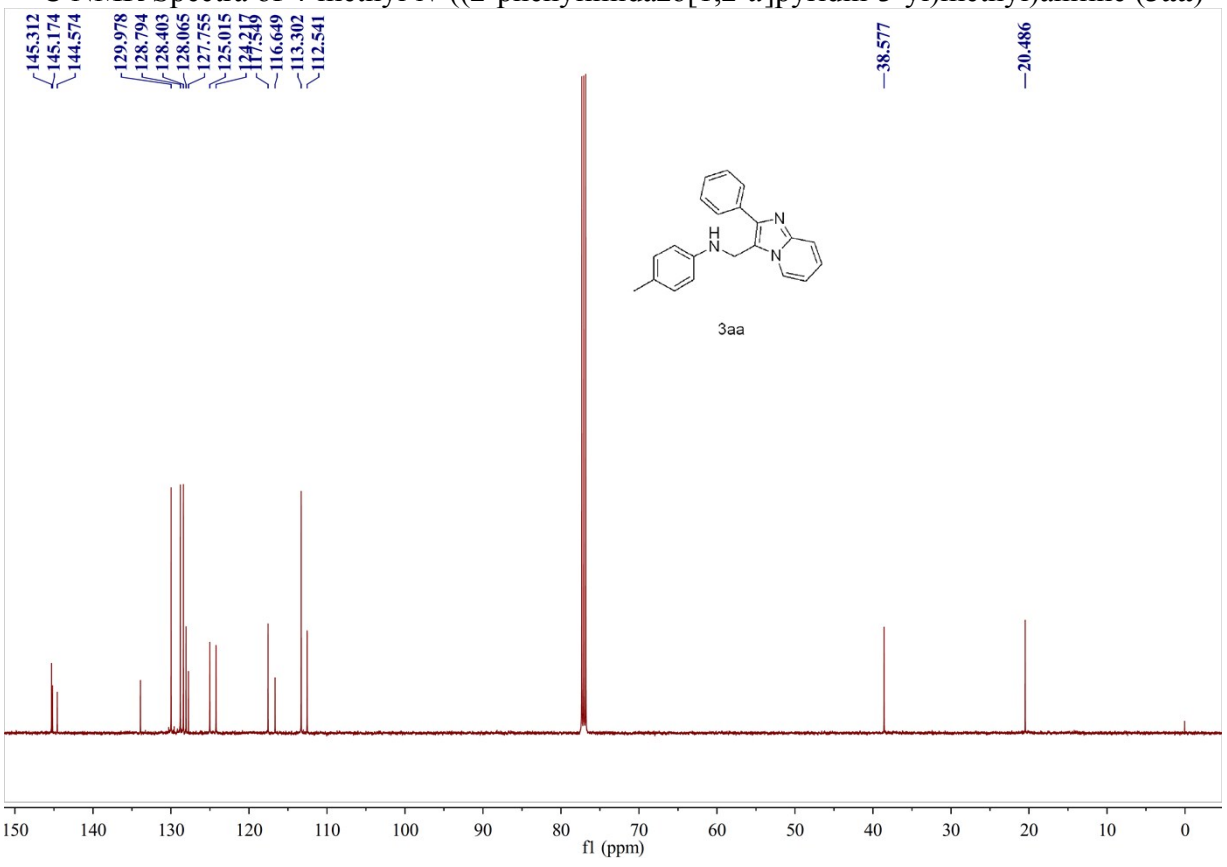
[2] P. Kaswan, A. Porter, K. Pericherla, M. Simone, S. Peters, A. Kumar and B. DeBoef, *Org. Lett.,* 2015, **17**, 5208.

5. ^{1}H NMR and ^{13}C NMR Spectra of Products

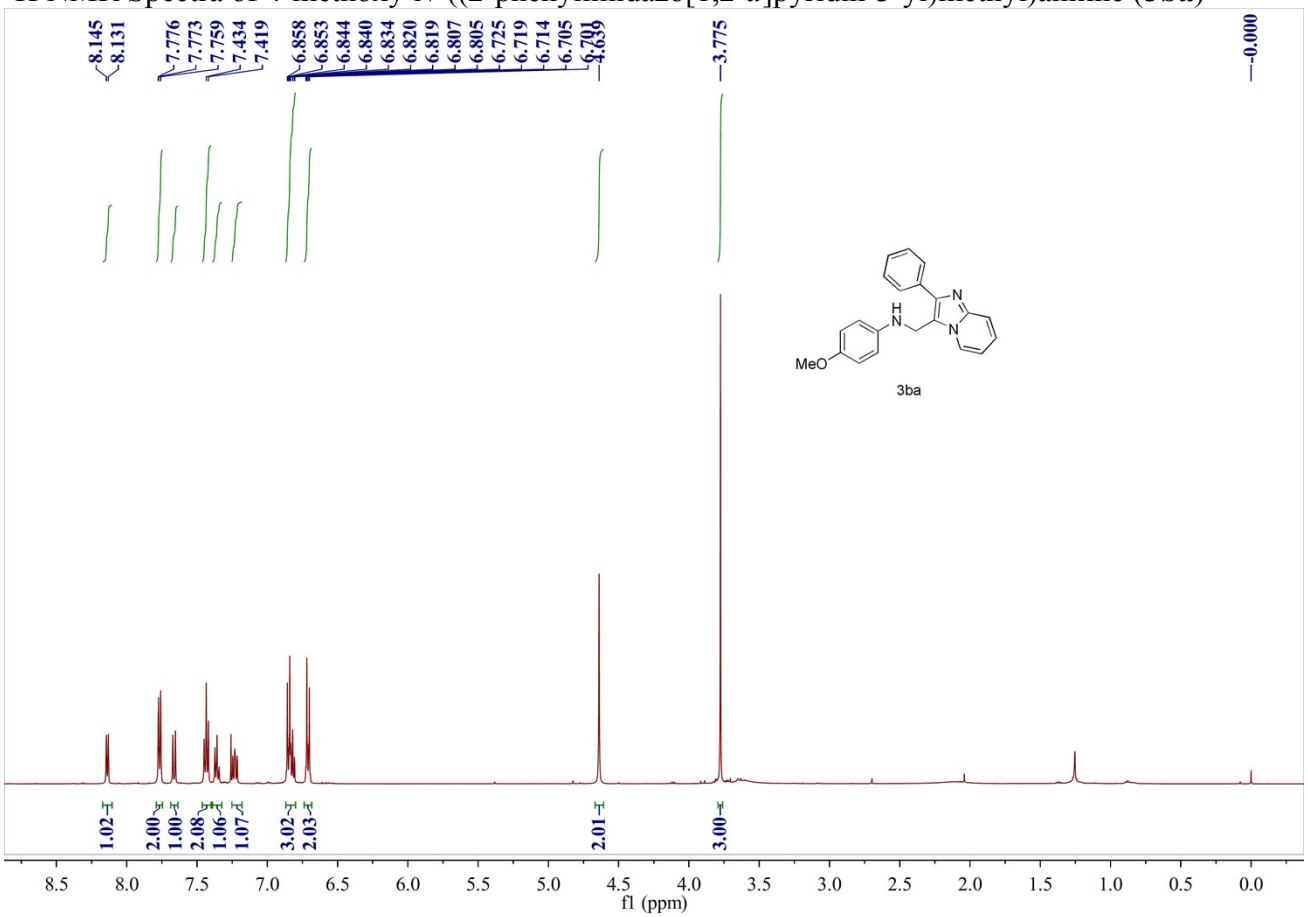
^{1}H NMR Spectra of 4-methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3aa**)



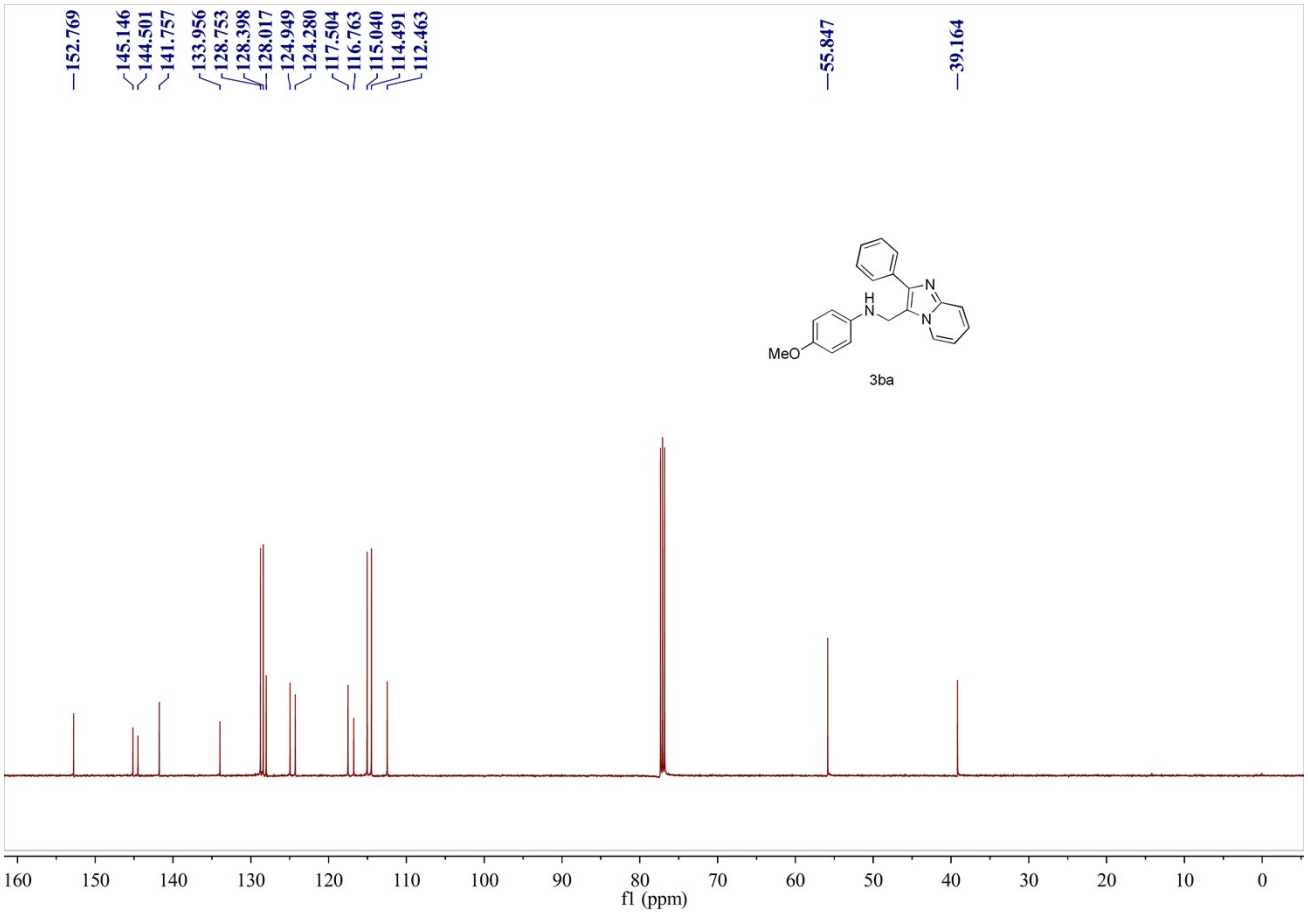
^{13}C NMR Spectra of 4-methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3aa**)



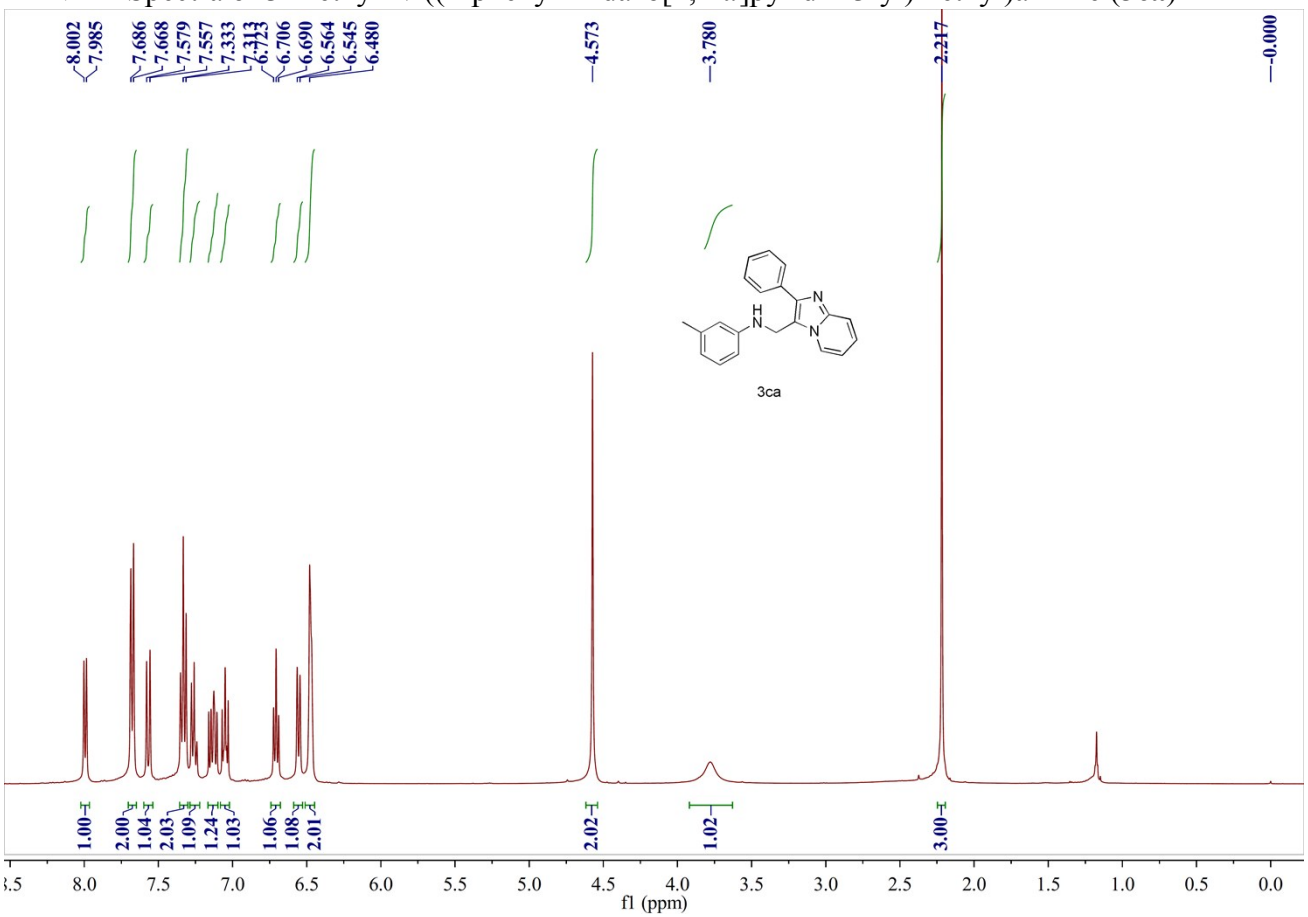
^{1}H NMR Spectra of 4-methoxy-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ba**)



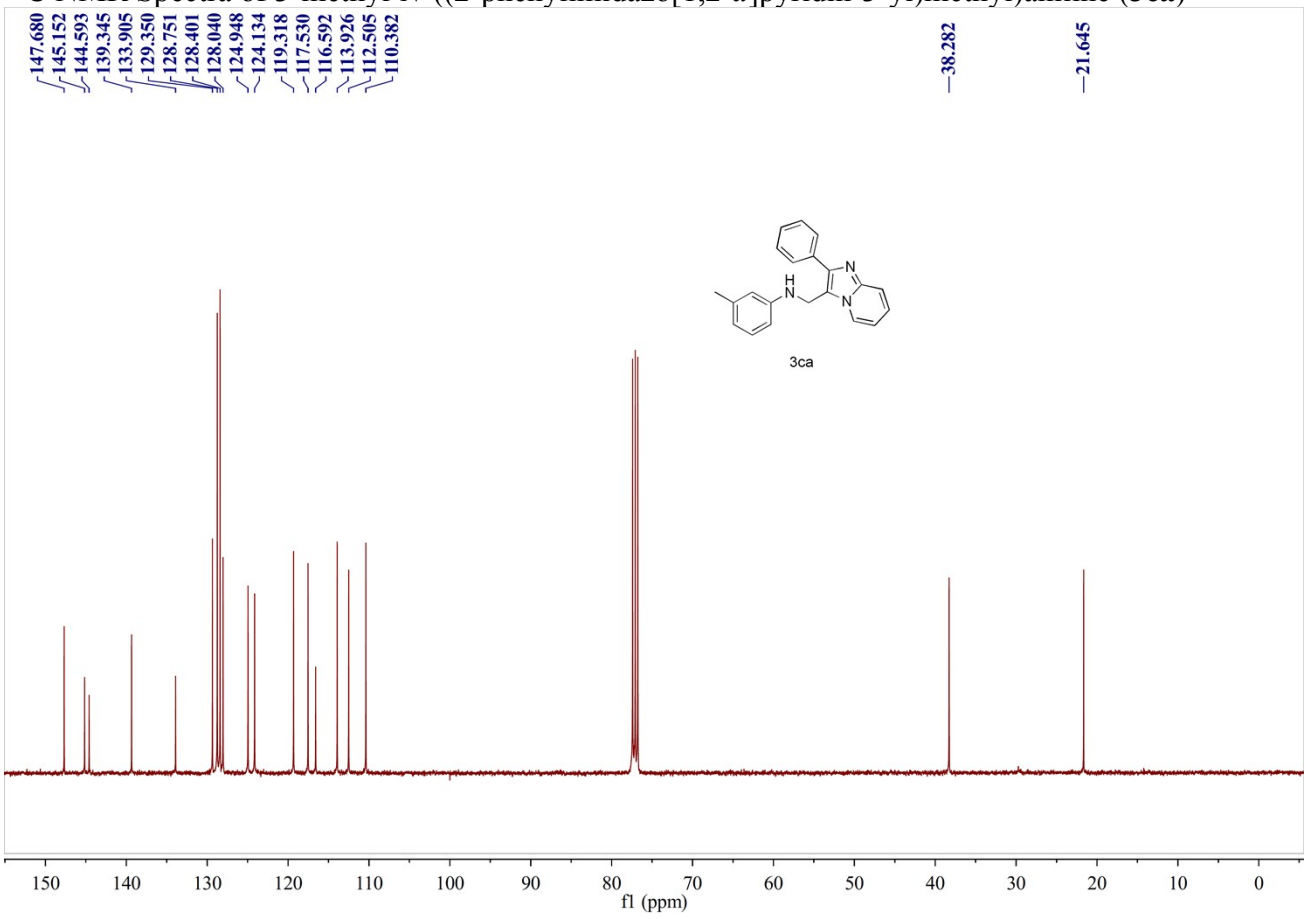
^{13}C NMR Spectra of 4-methoxy-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ba**)



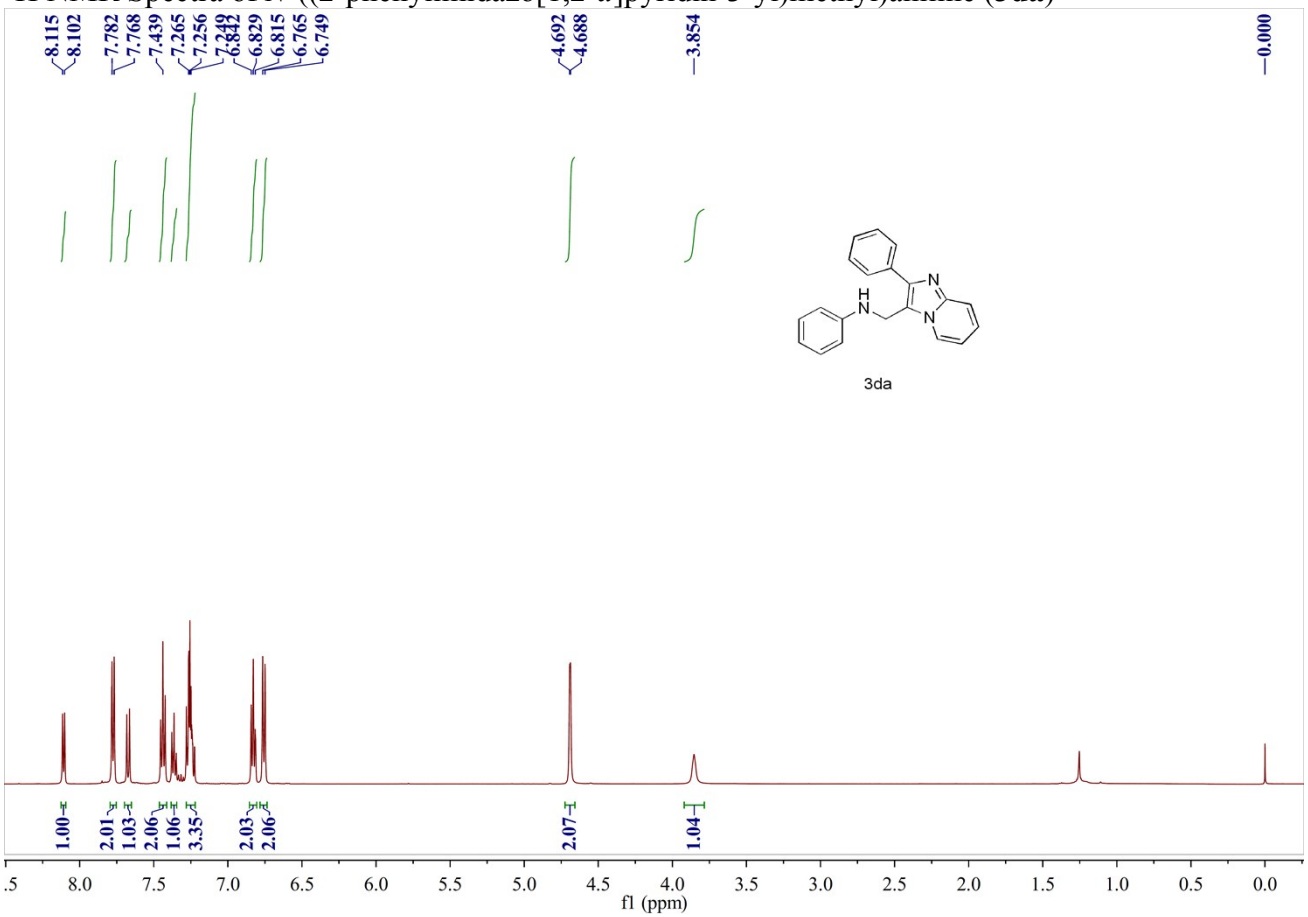
^{1}H NMR Spectra of 3-methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ca**)



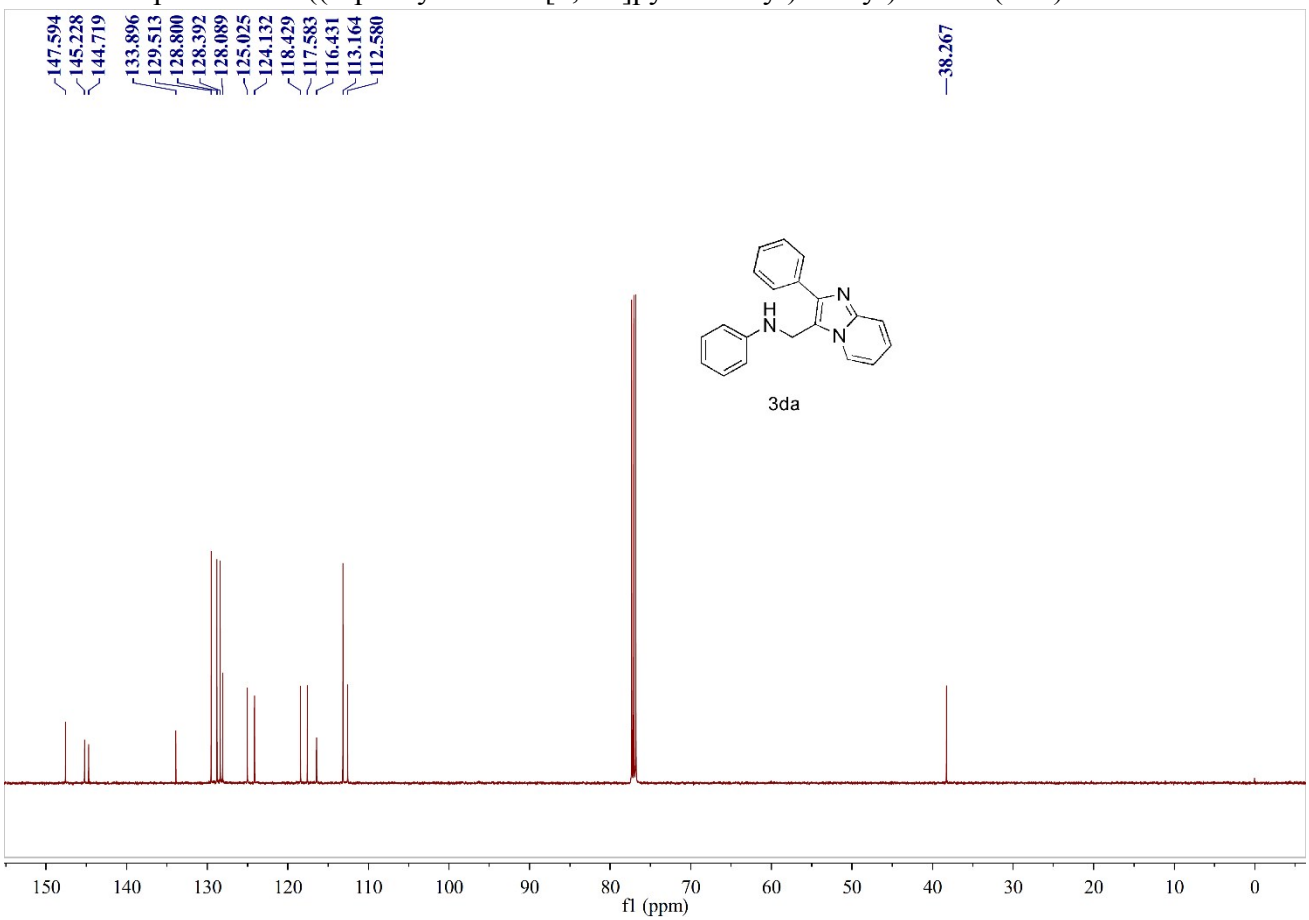
^{13}C NMR Spectra of 3-methyl-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ca**)



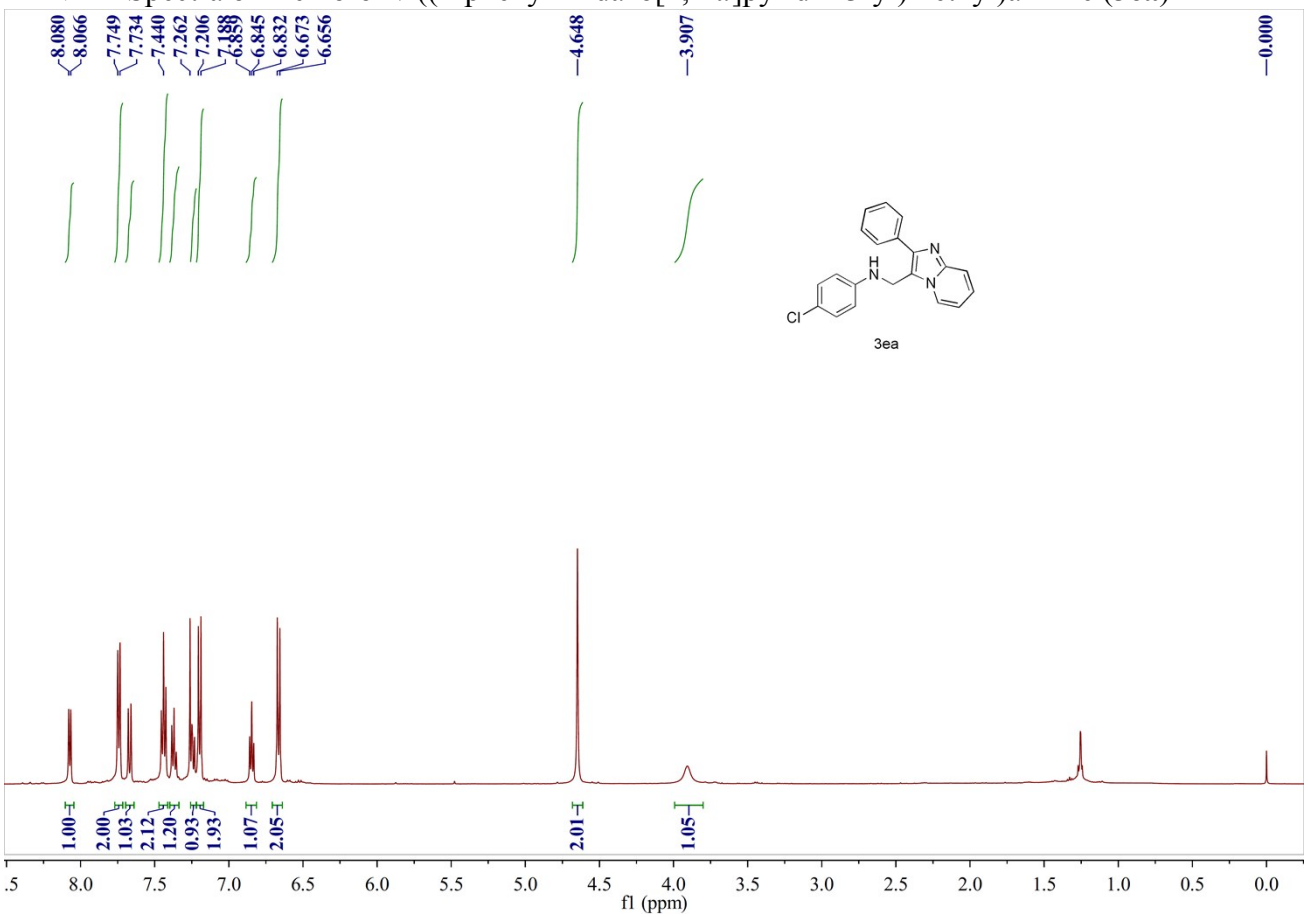
^{1}H NMR Spectra of *N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3da**)



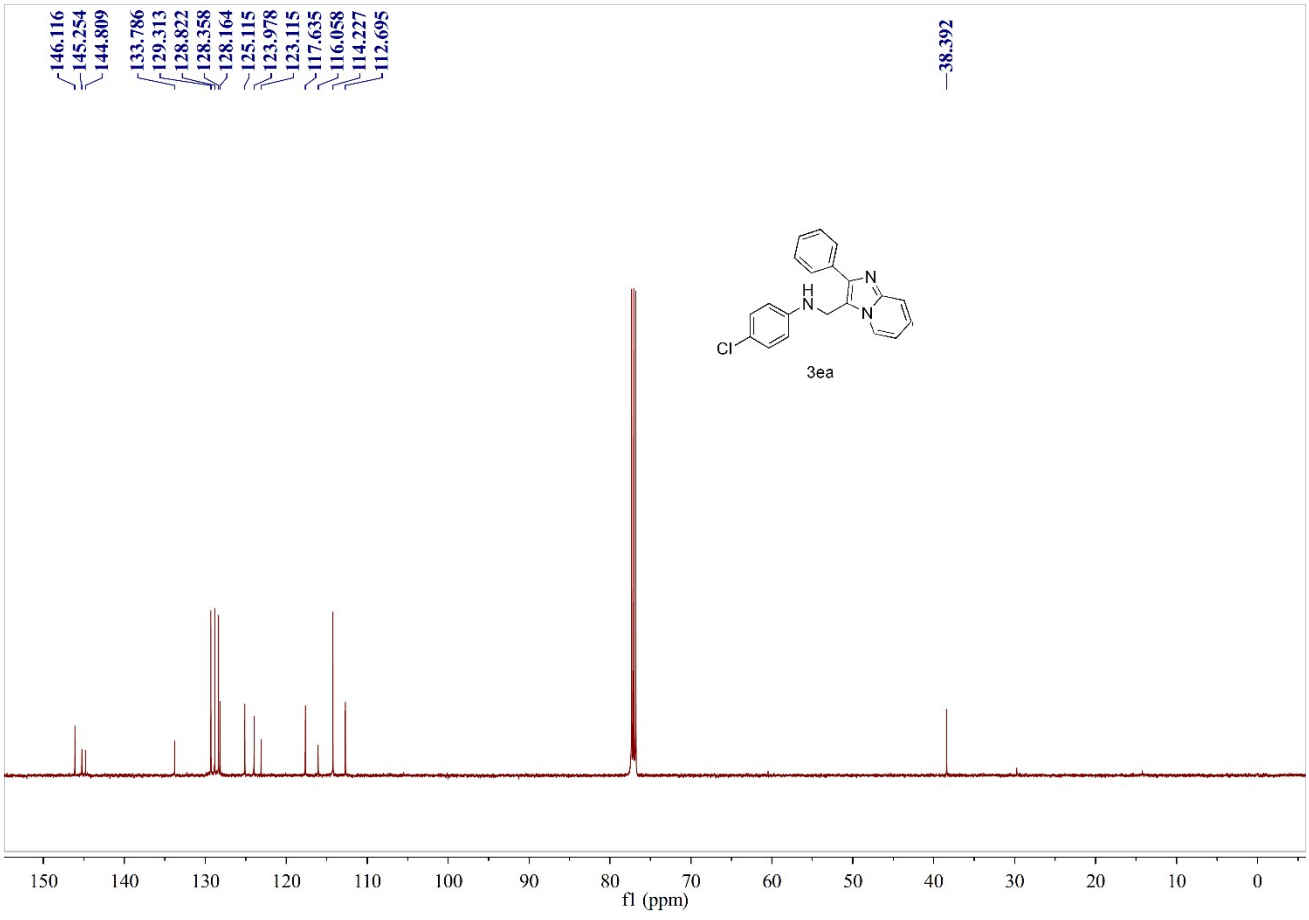
^{13}C NMR Spectra of *N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3da**)



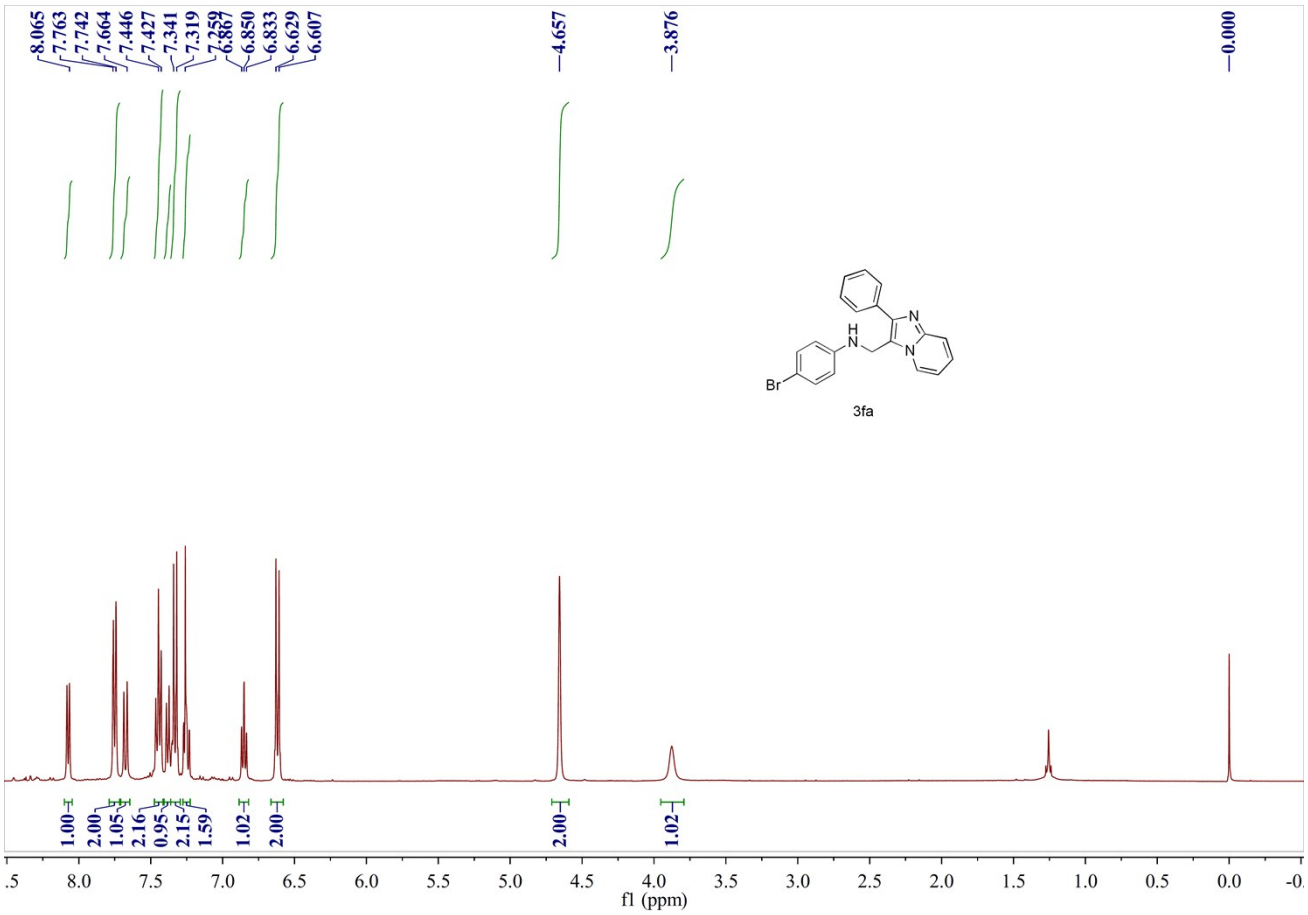
^{1}H NMR Spectra of 4-chloro-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ea**)



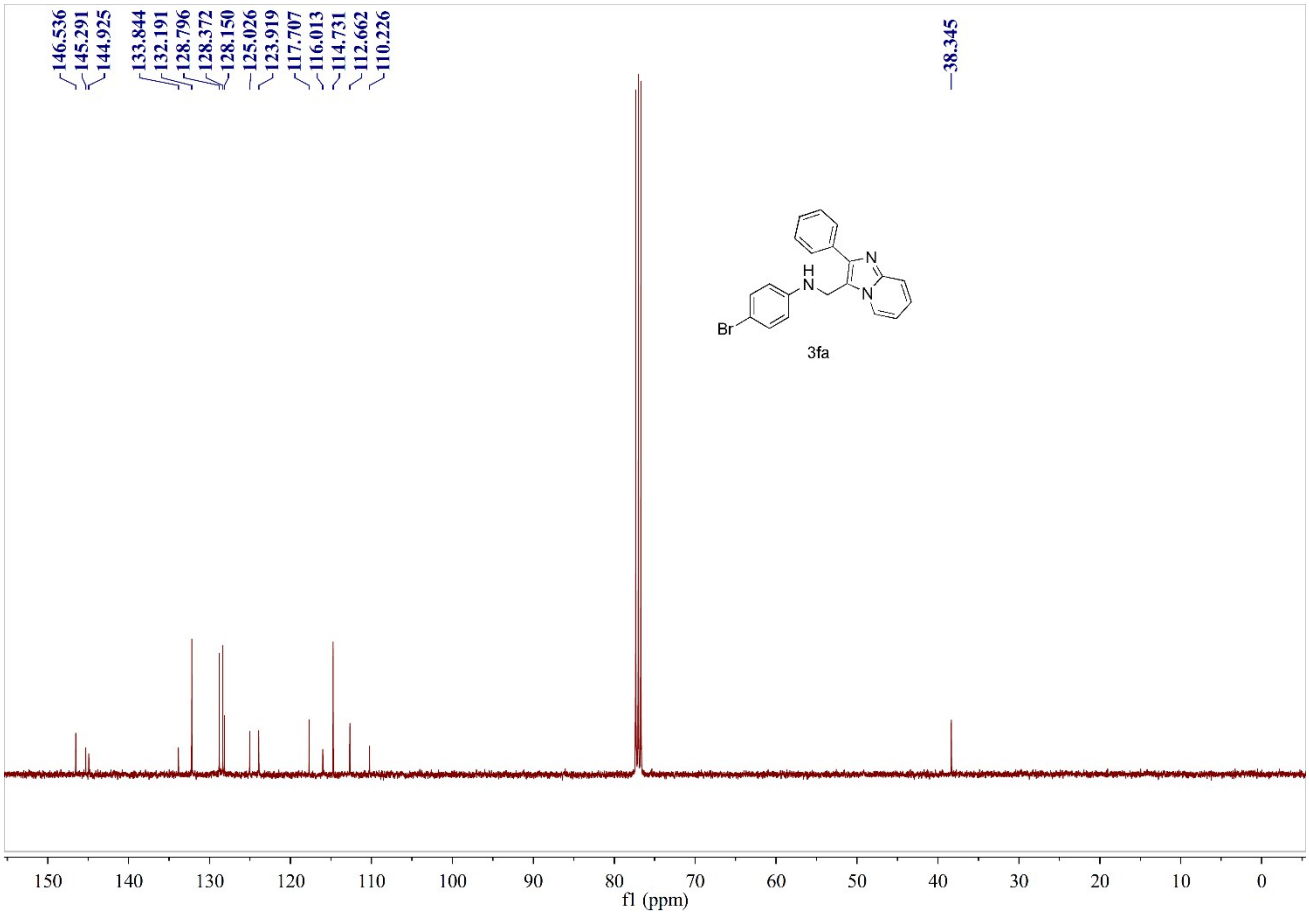
^{13}C NMR Spectra of 4-chloro-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ea**)



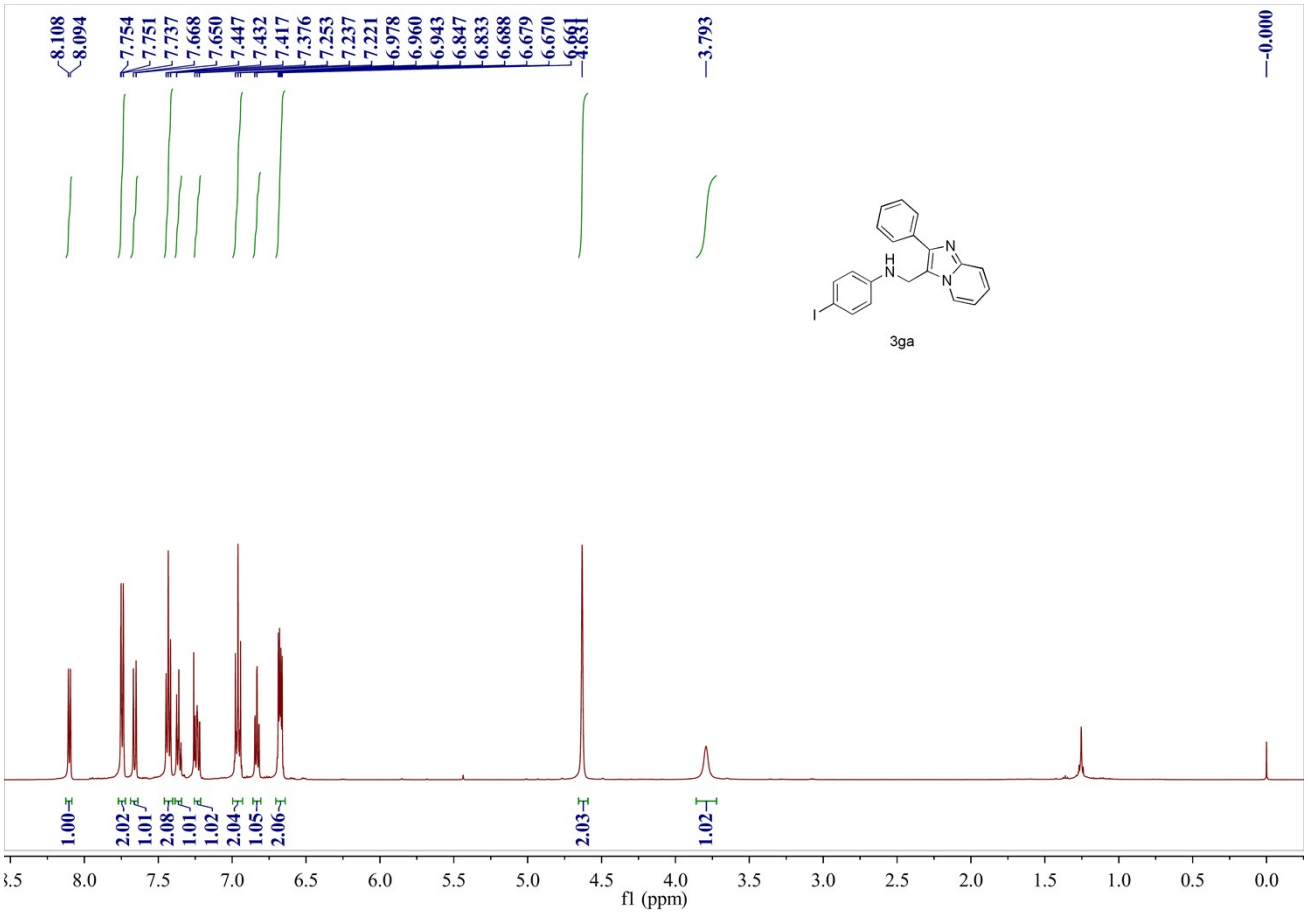
^{1}H NMR Spectra of 4-bromo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3fa**)



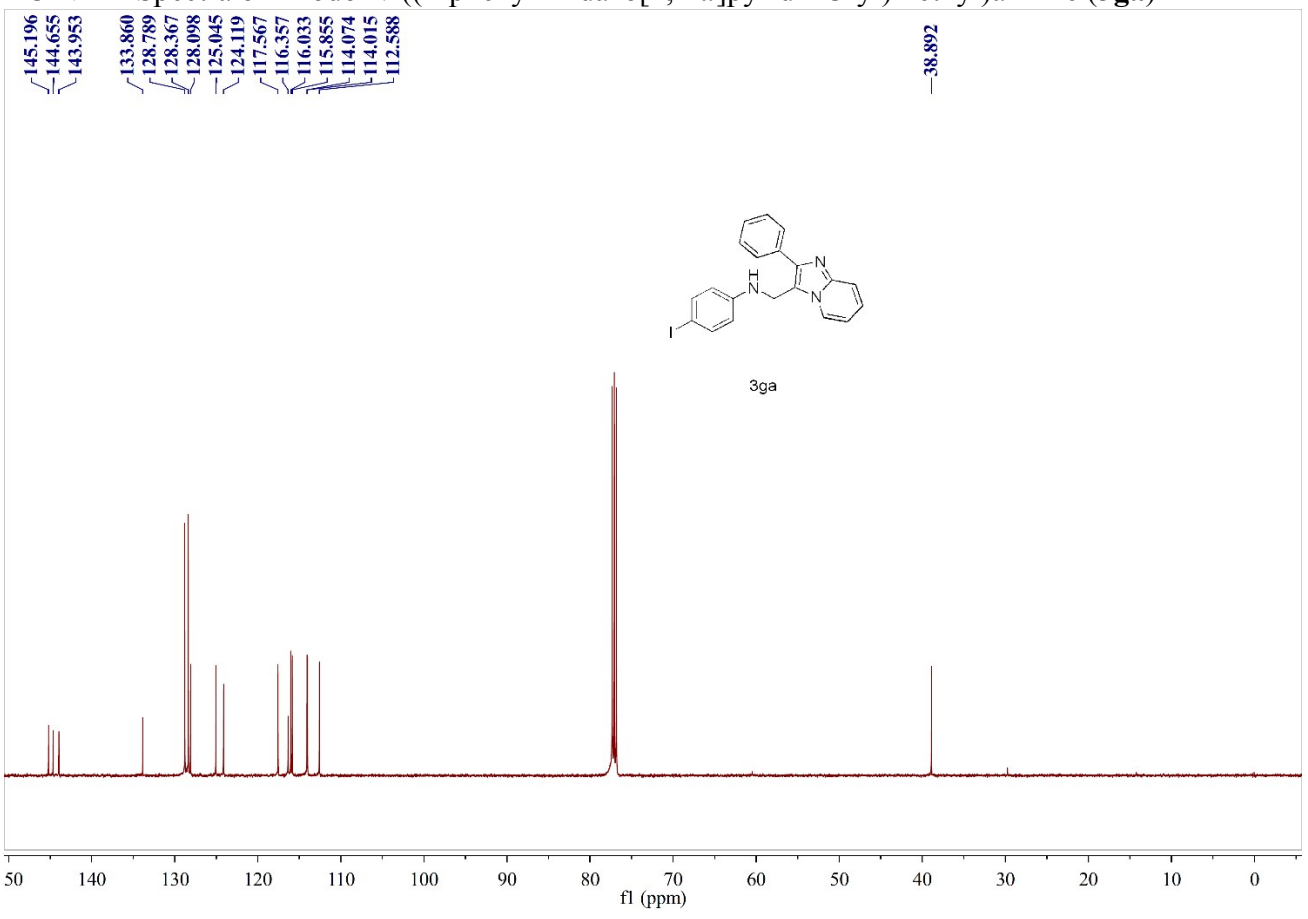
^{13}C NMR Spectra of 4-bromo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3fa**)



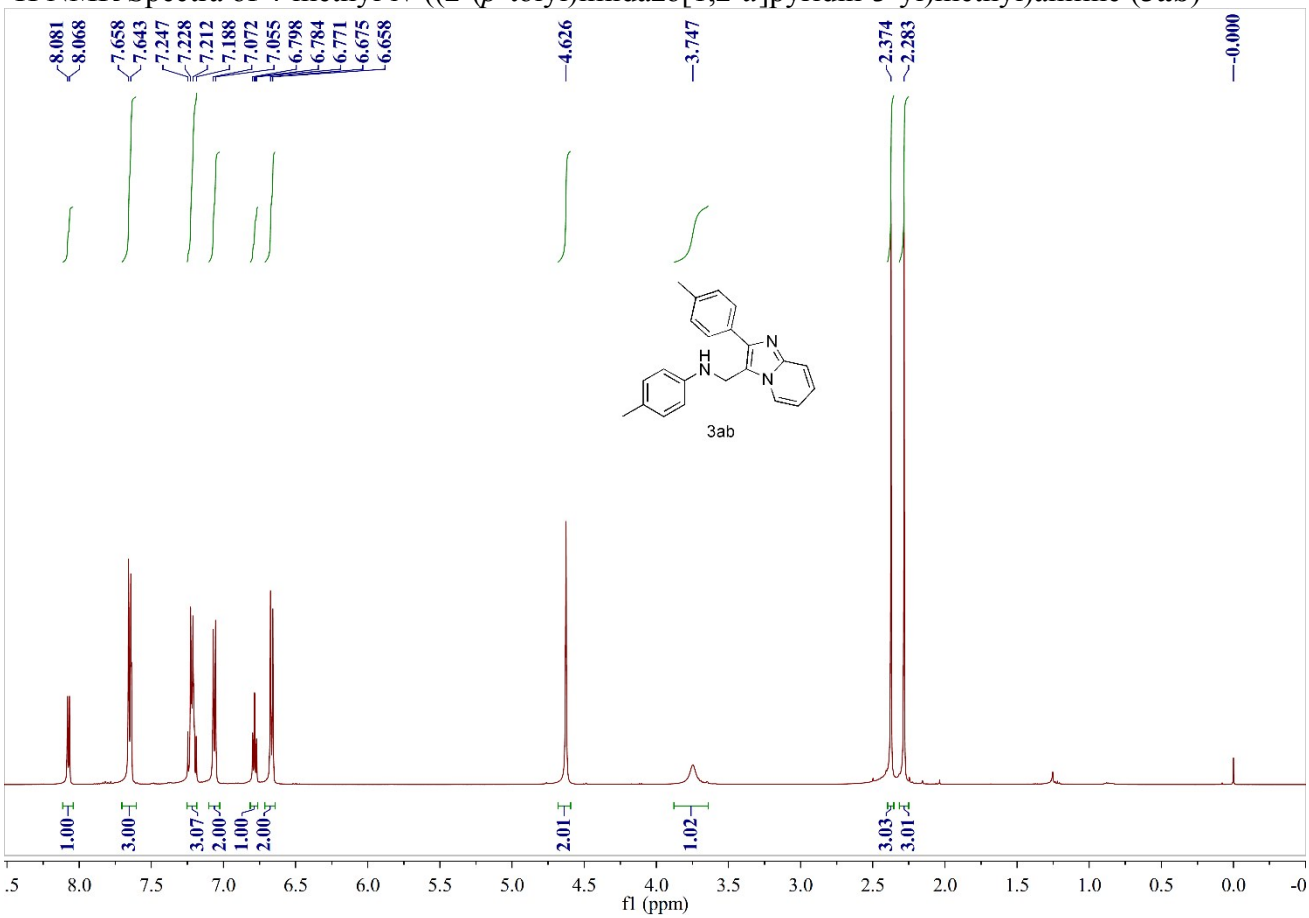
^{1}H NMR Spectra of 4-iodo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ga**)



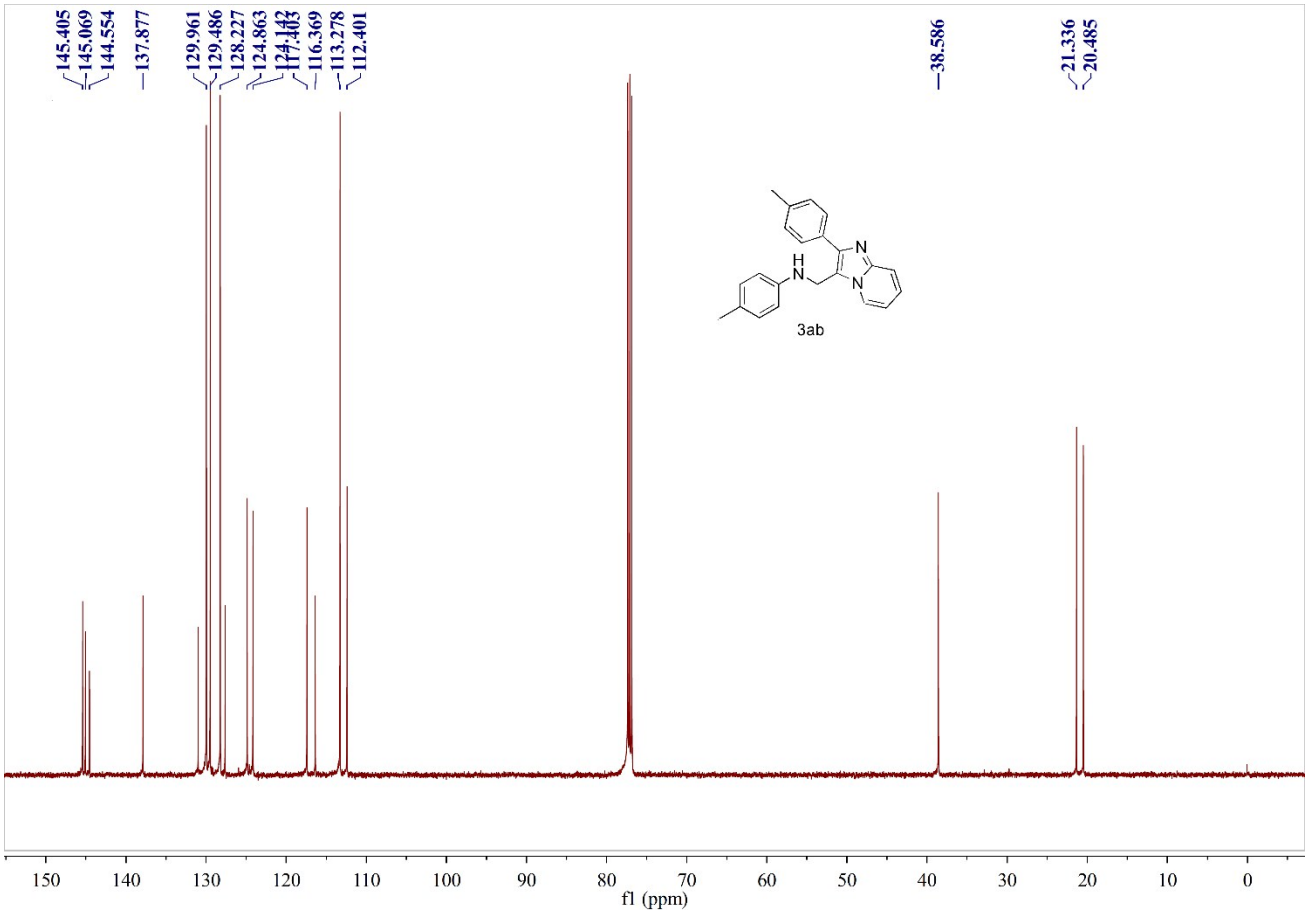
^{13}C NMR Spectra of 4-iodo-*N*-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ga**)



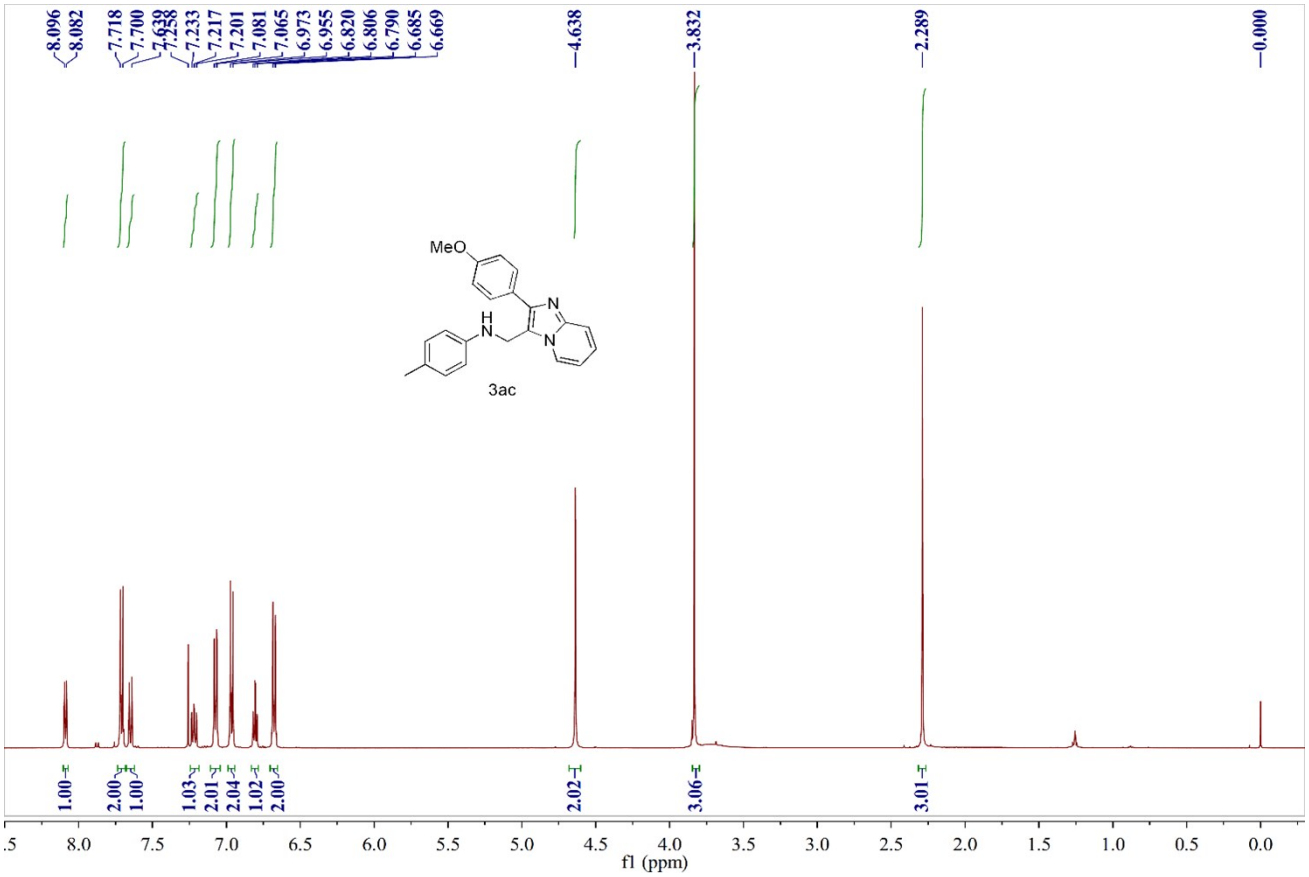
^{1}H NMR Spectra of 4-methyl-*N*-((2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ab**)



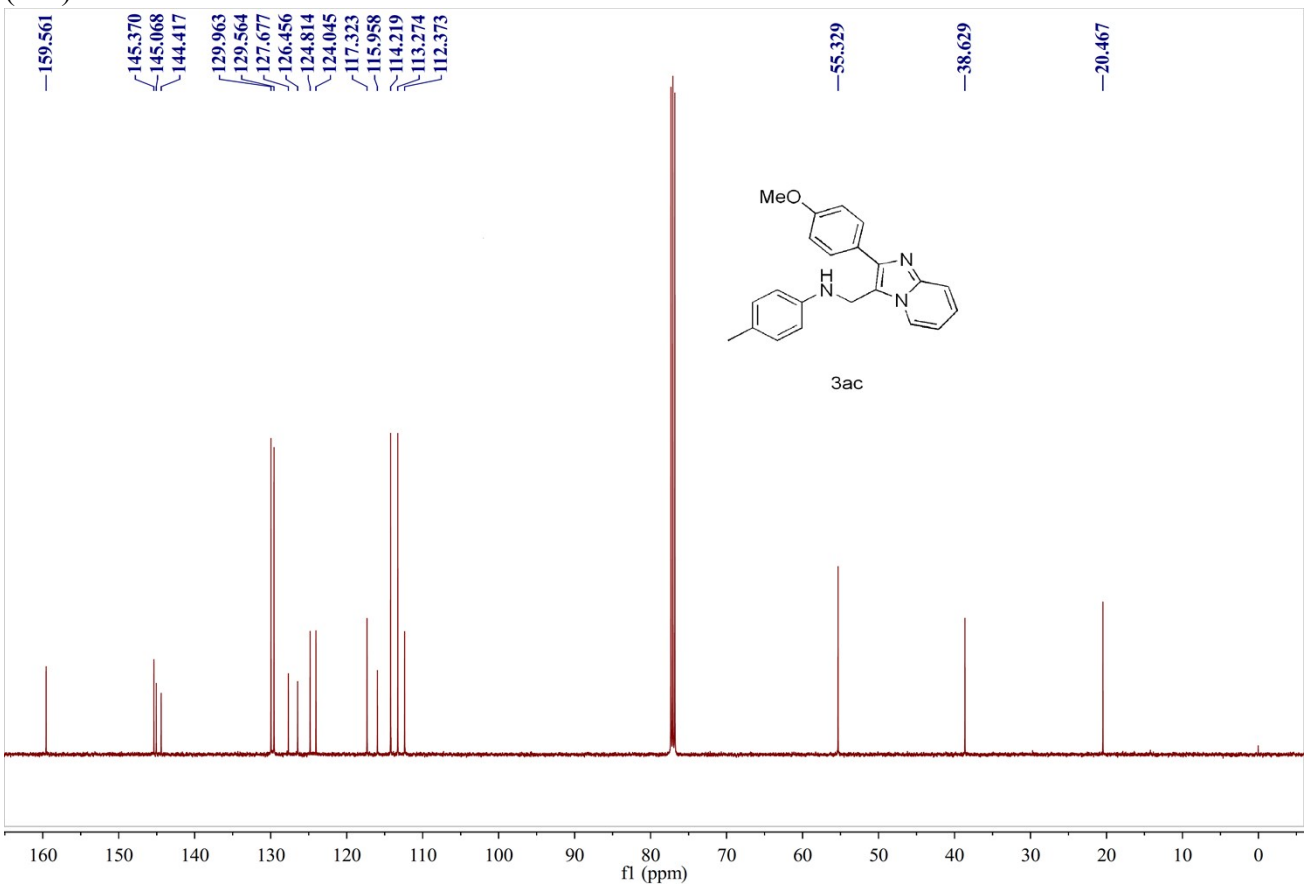
^{13}C NMR Spectra of 4-methyl-*N*-((2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ab**)



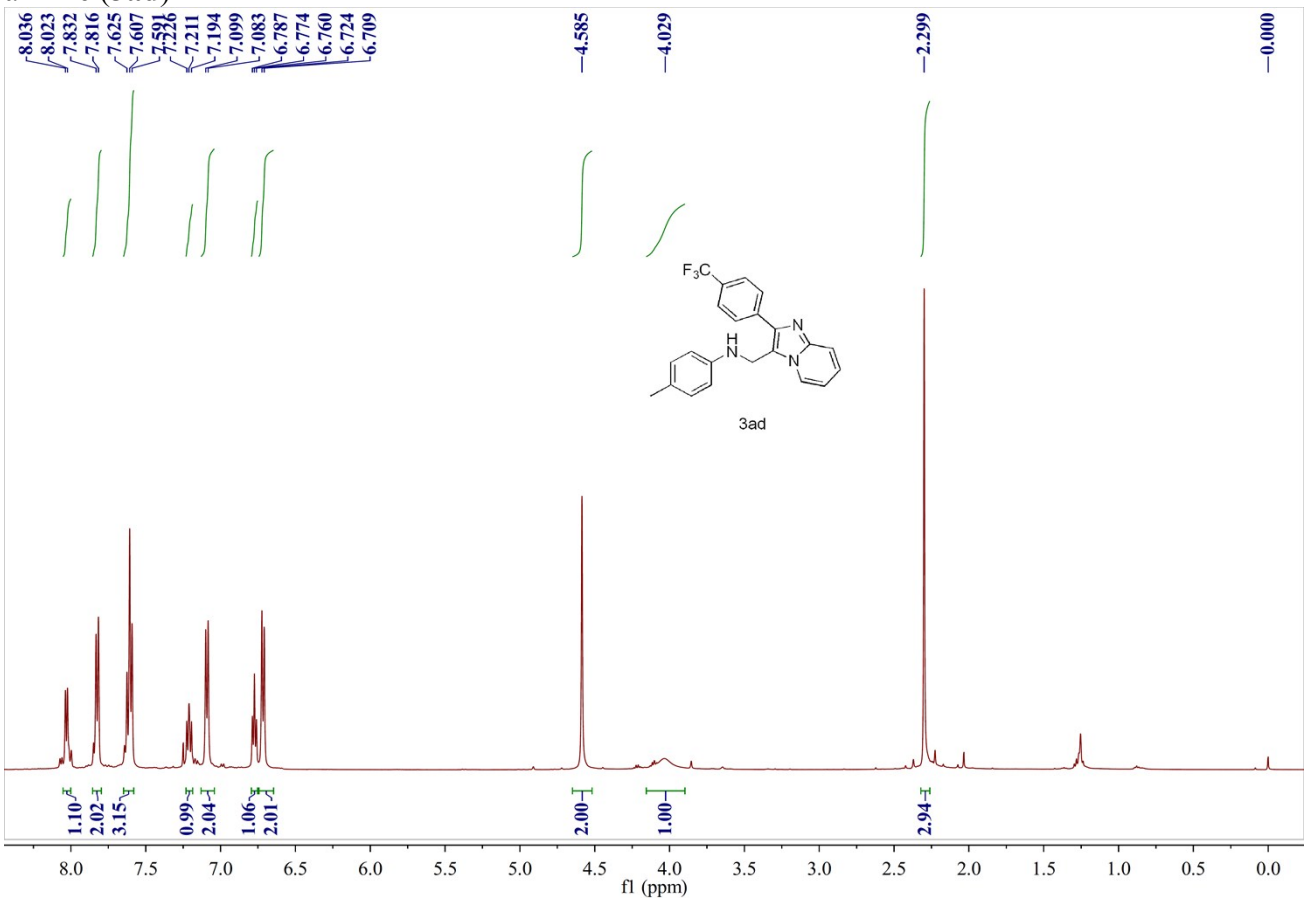
^{1}H NMR Spectra of *N*-((2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ac**)



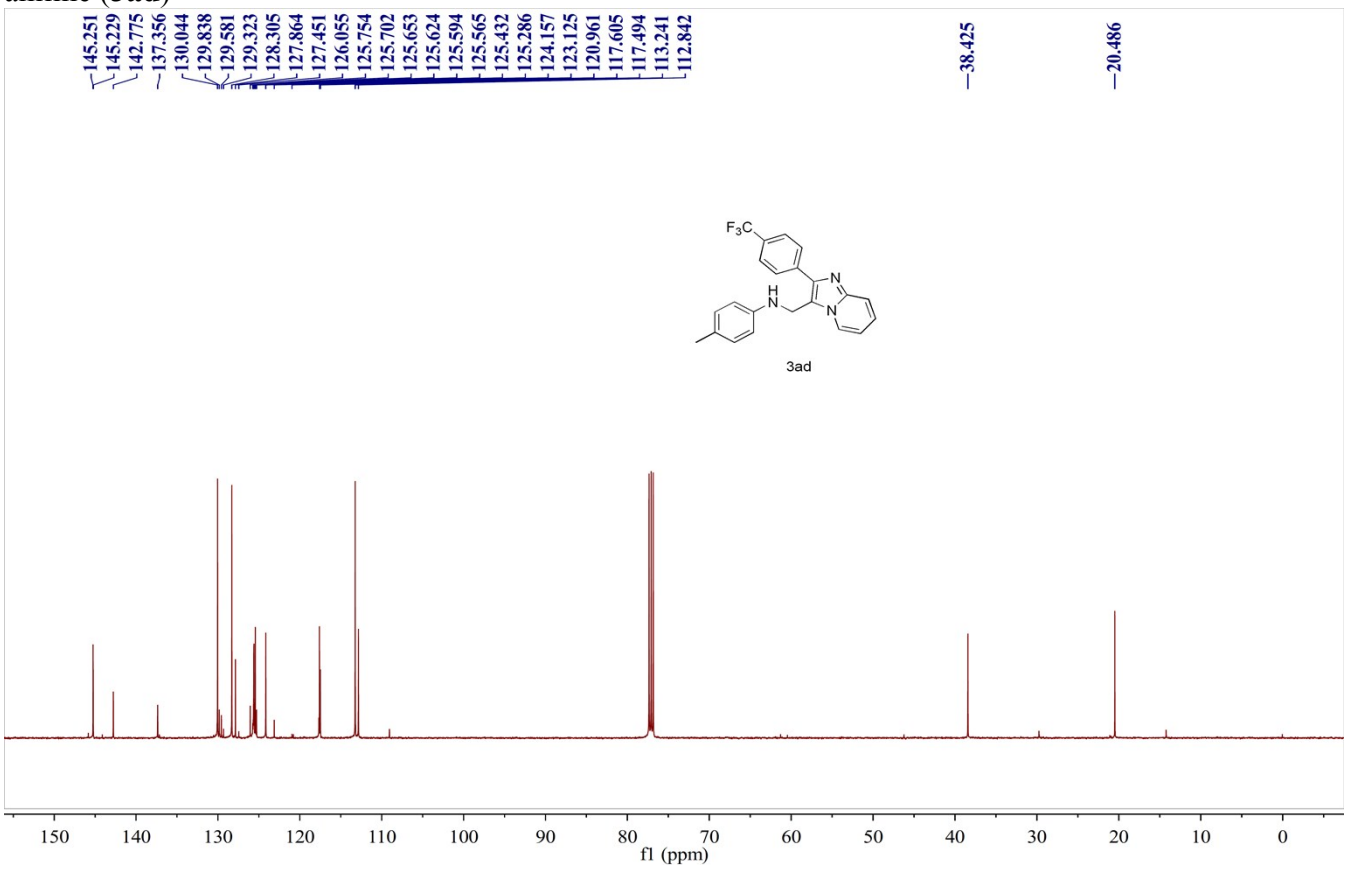
^{13}C NMR Spectra of *N*-((2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ac**)



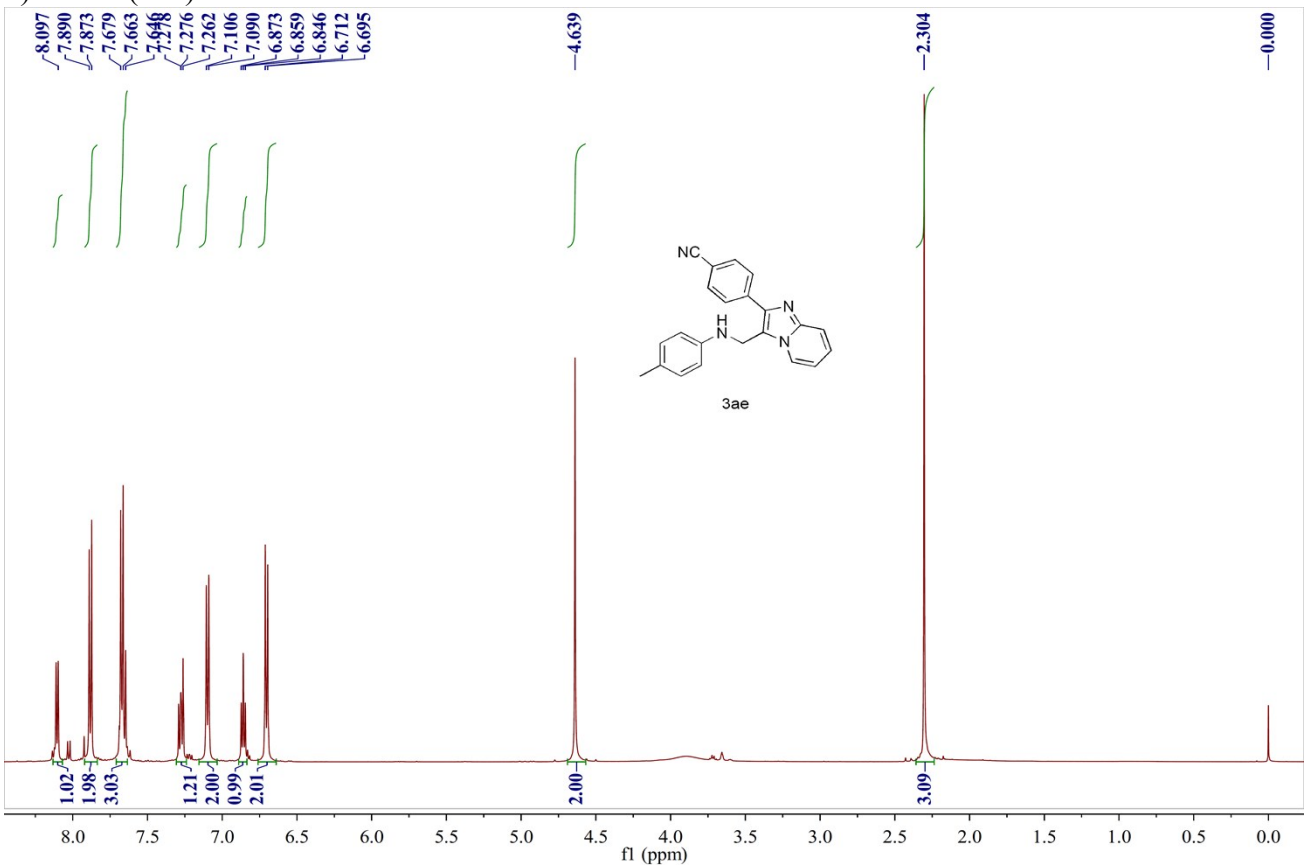
^{1}H NMR Spectra of 4-methyl-*N*-((2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-aniline (**3ad**)



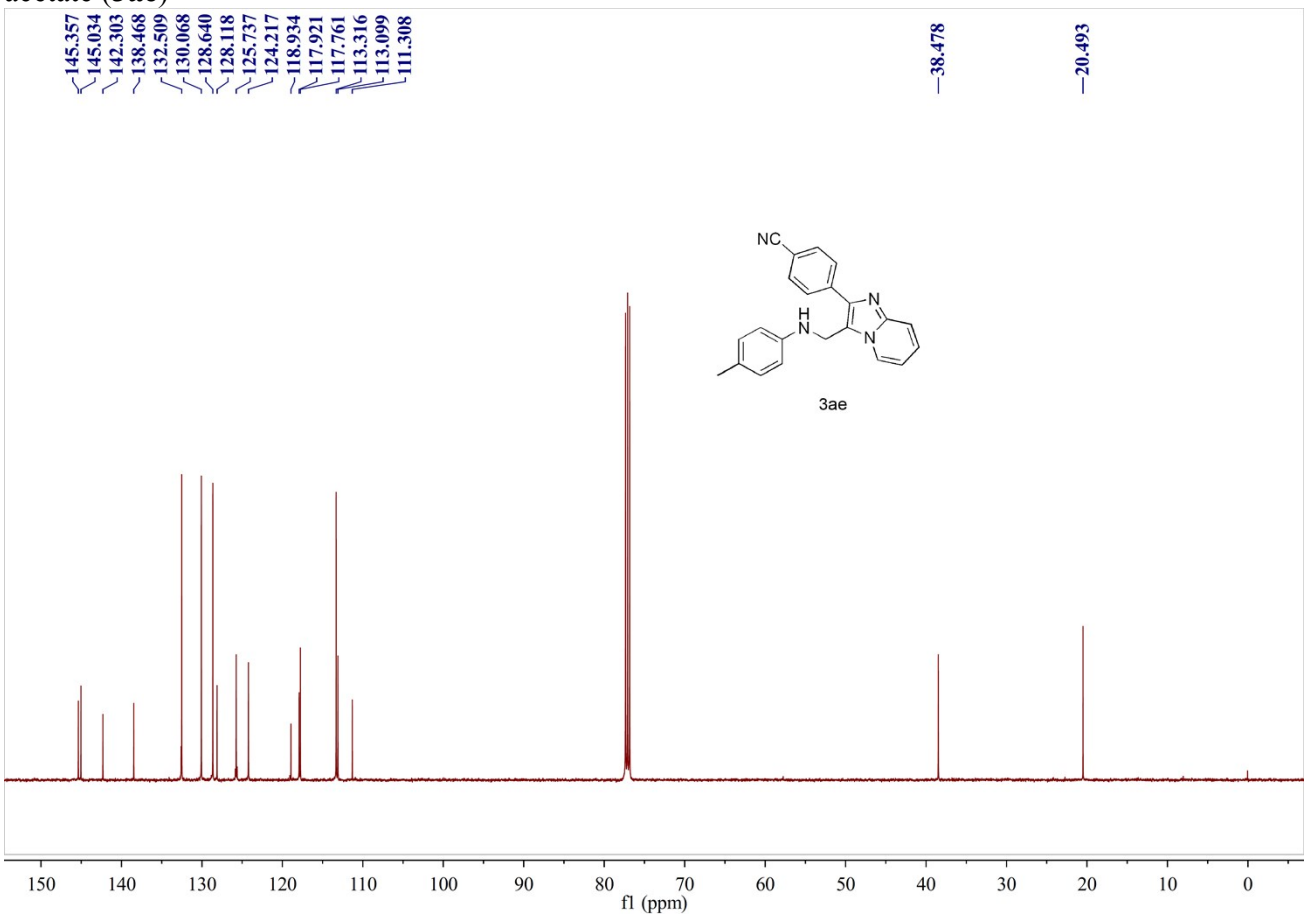
^{13}C NMR Spectra of 4-methyl-*N*-((2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-aniline (**3ad**)



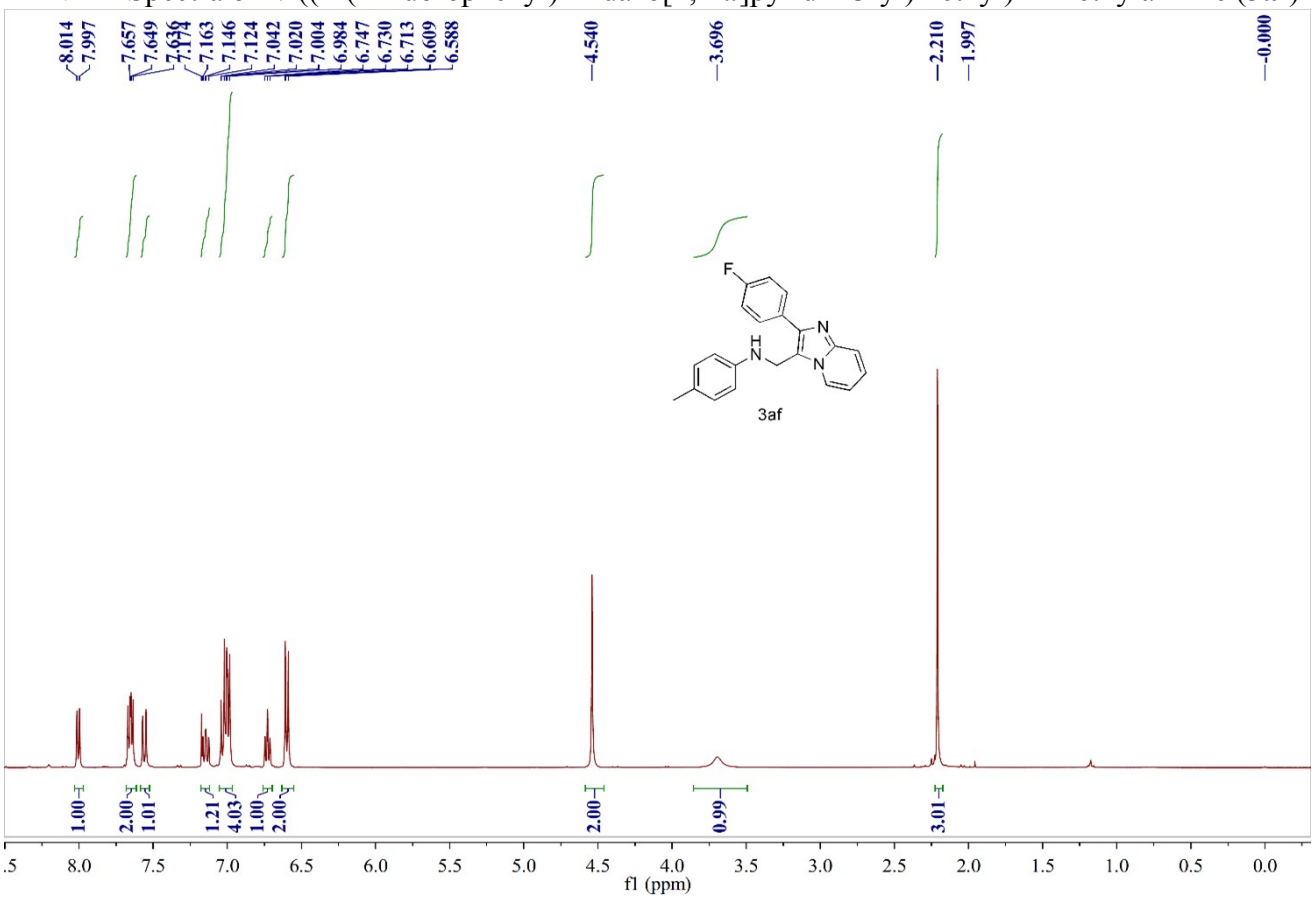
^{1}H NMR Spectra of Ethyl 2-(6,6-dimethyl-2,4-dioxo-3-azabicyclo[3.1.0]hexan-3-yl)-2-(p-tolylamino)acetate (**3ae**)



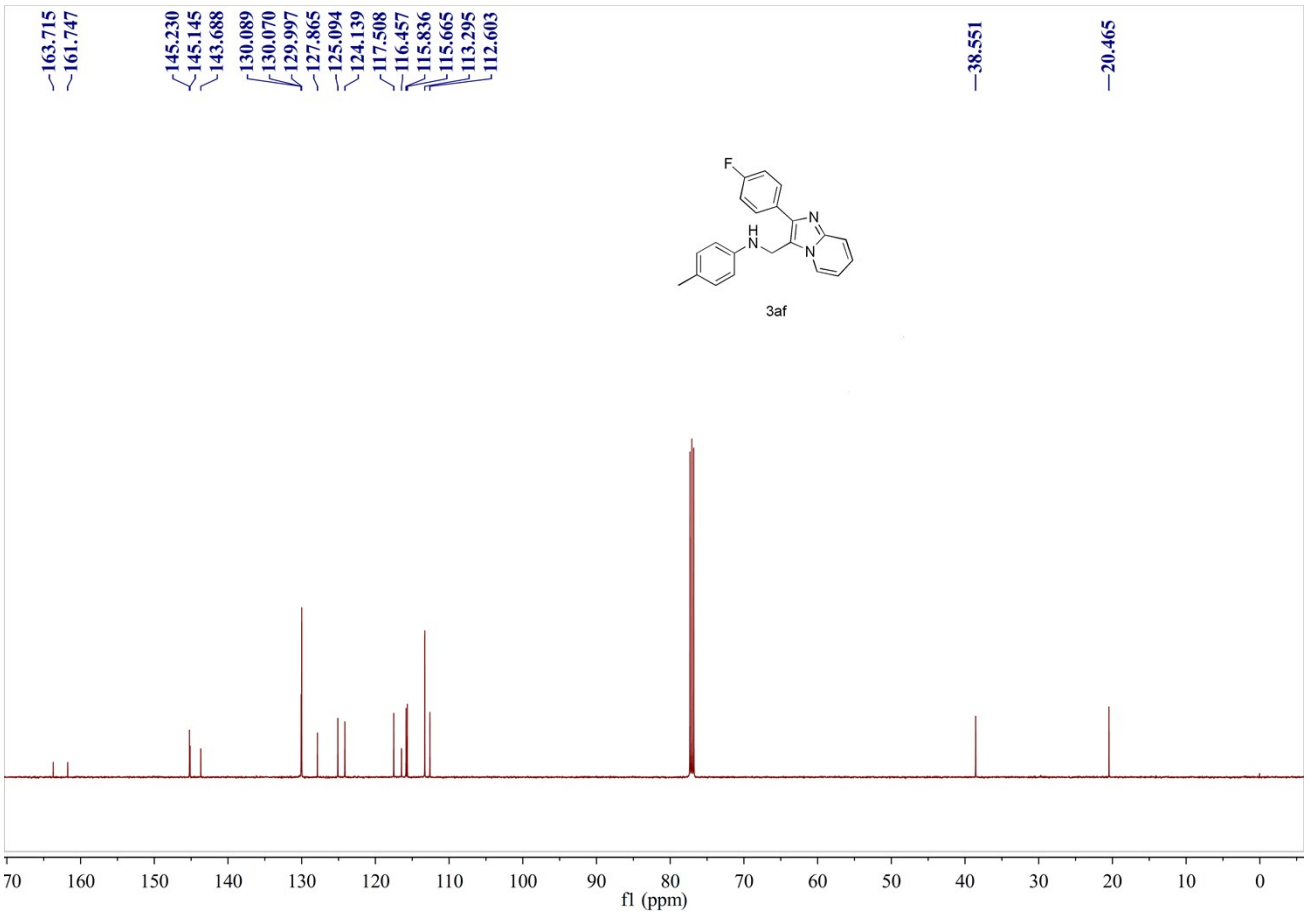
^{13}C NMR Spectra of 2-(6,6-dimethyl-2,4-dioxo-3-azabicyclo[3.1.0]hexan-3-yl)-2-(p-tolylamino)-acetate (**3ae**)



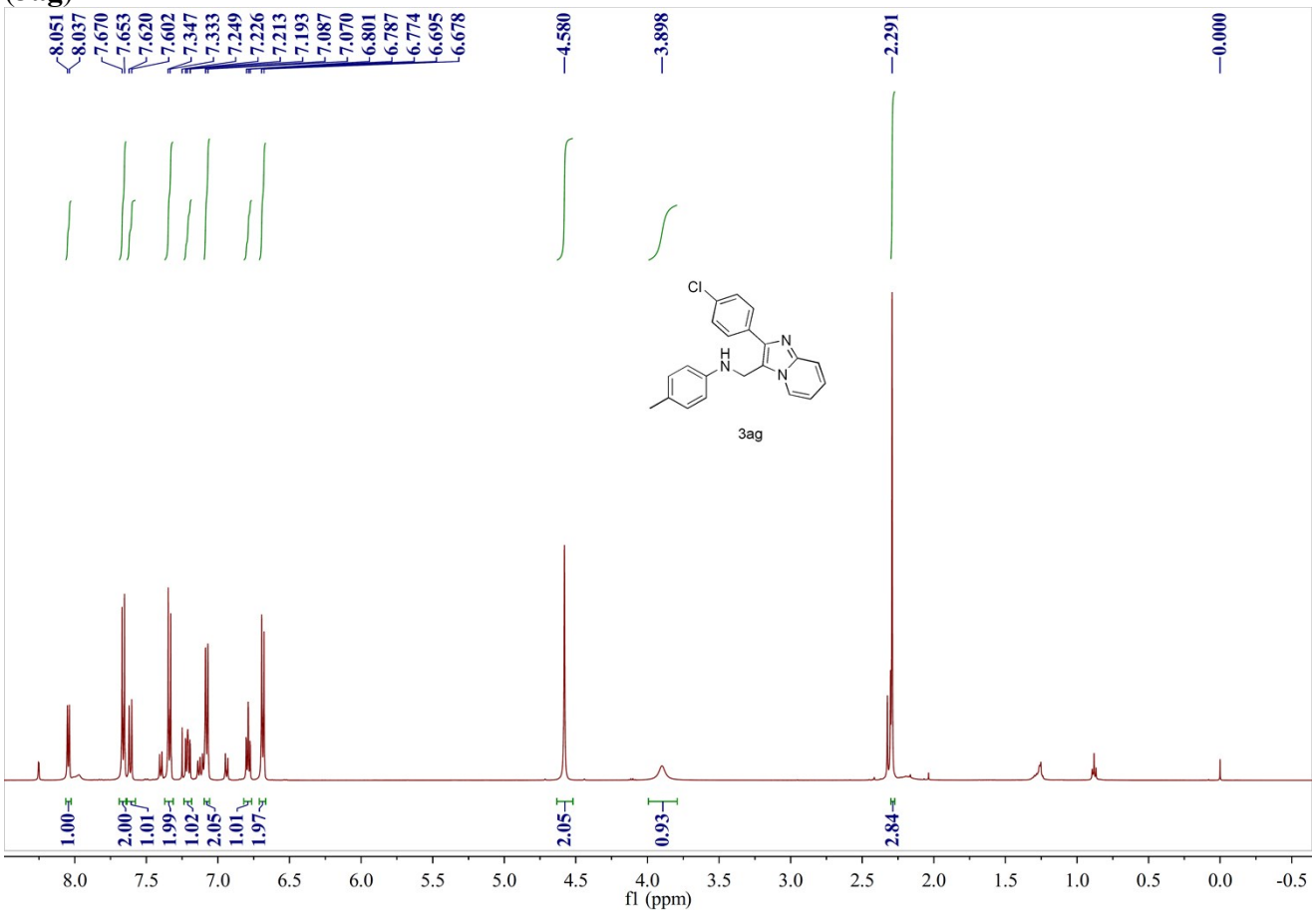
^{1}H NMR Spectra of *N*-((2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3af**)



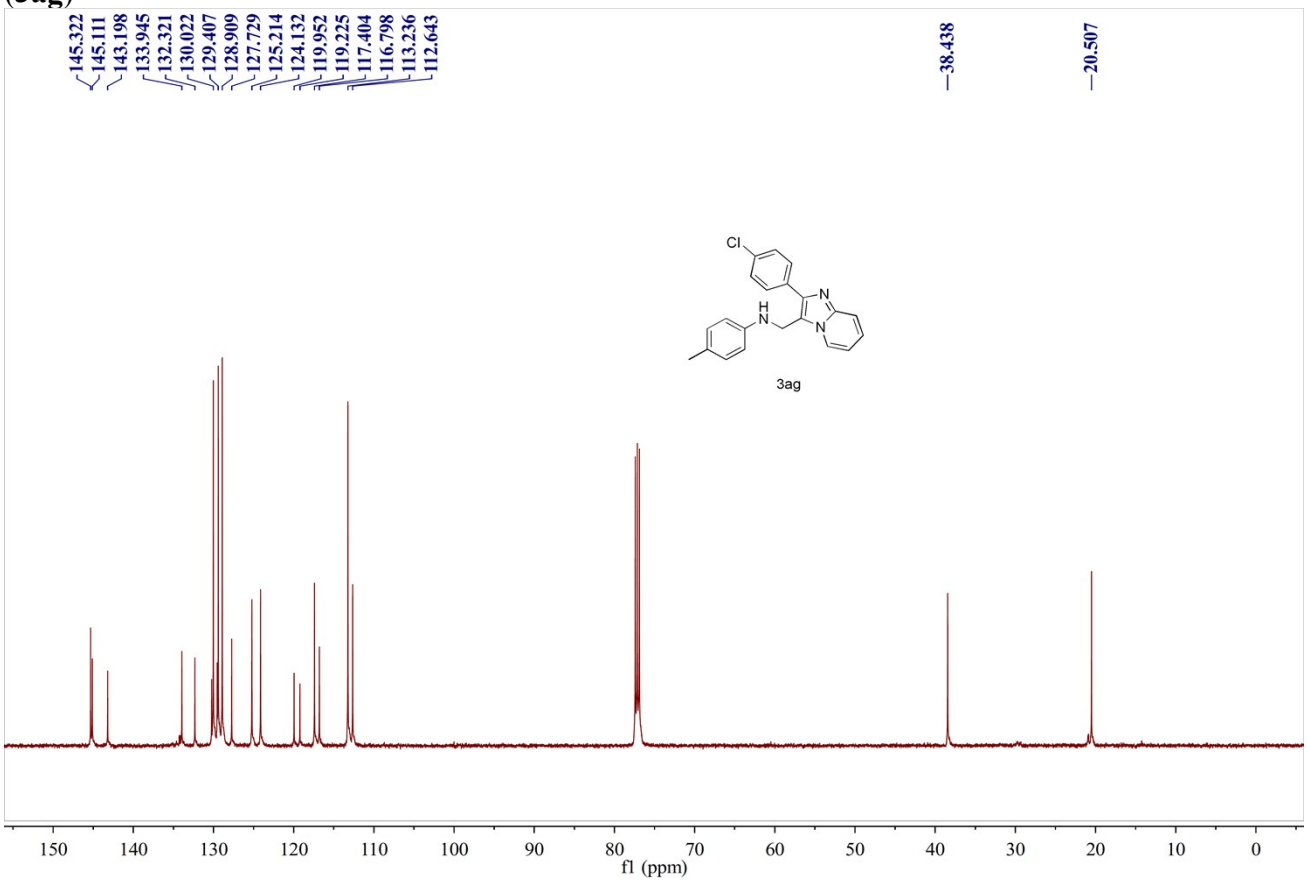
^{13}C NMR Spectra of *N*-((2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline(**3af**)



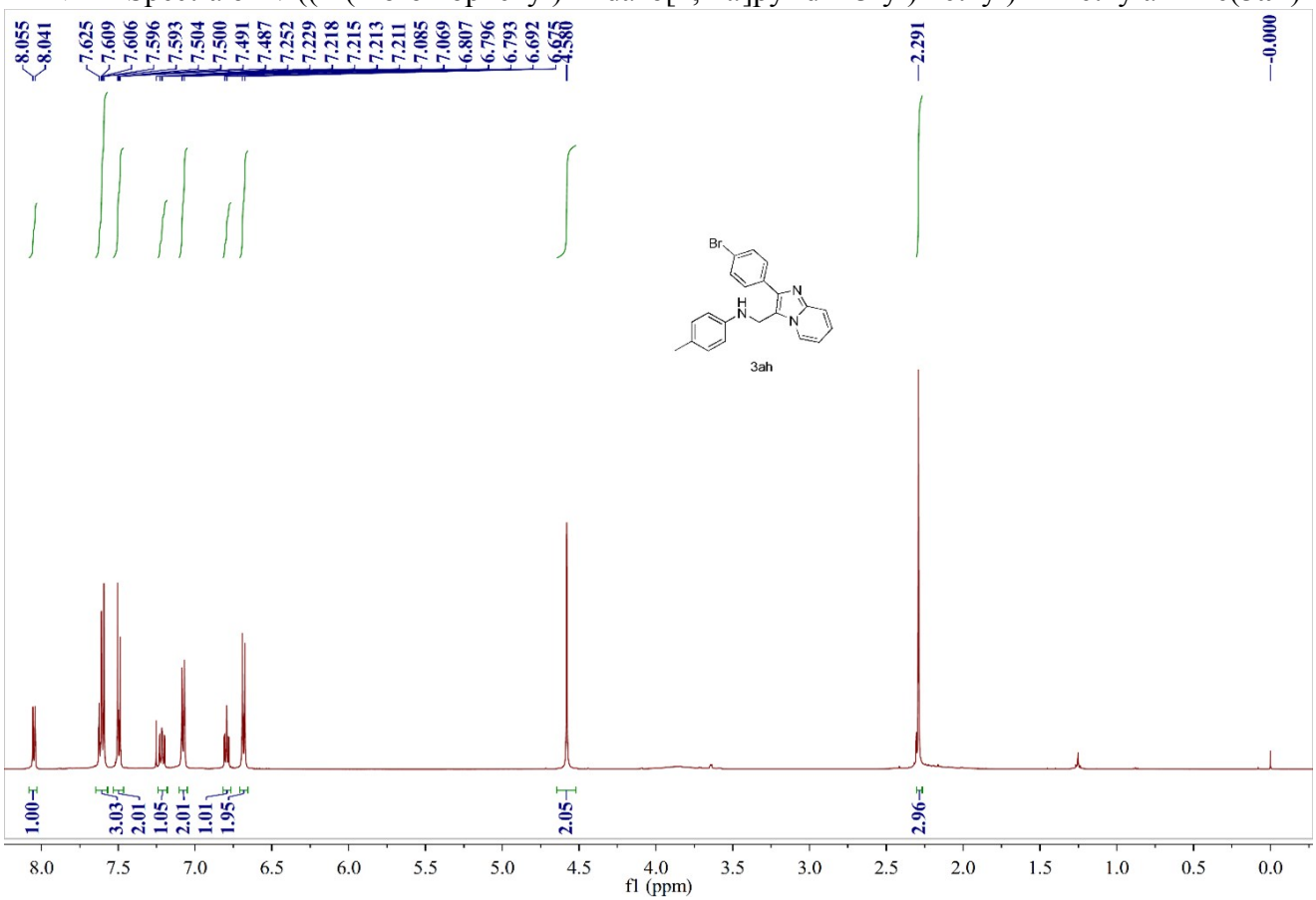
^{1}H NMR Spectra of *N*-((2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ag**)



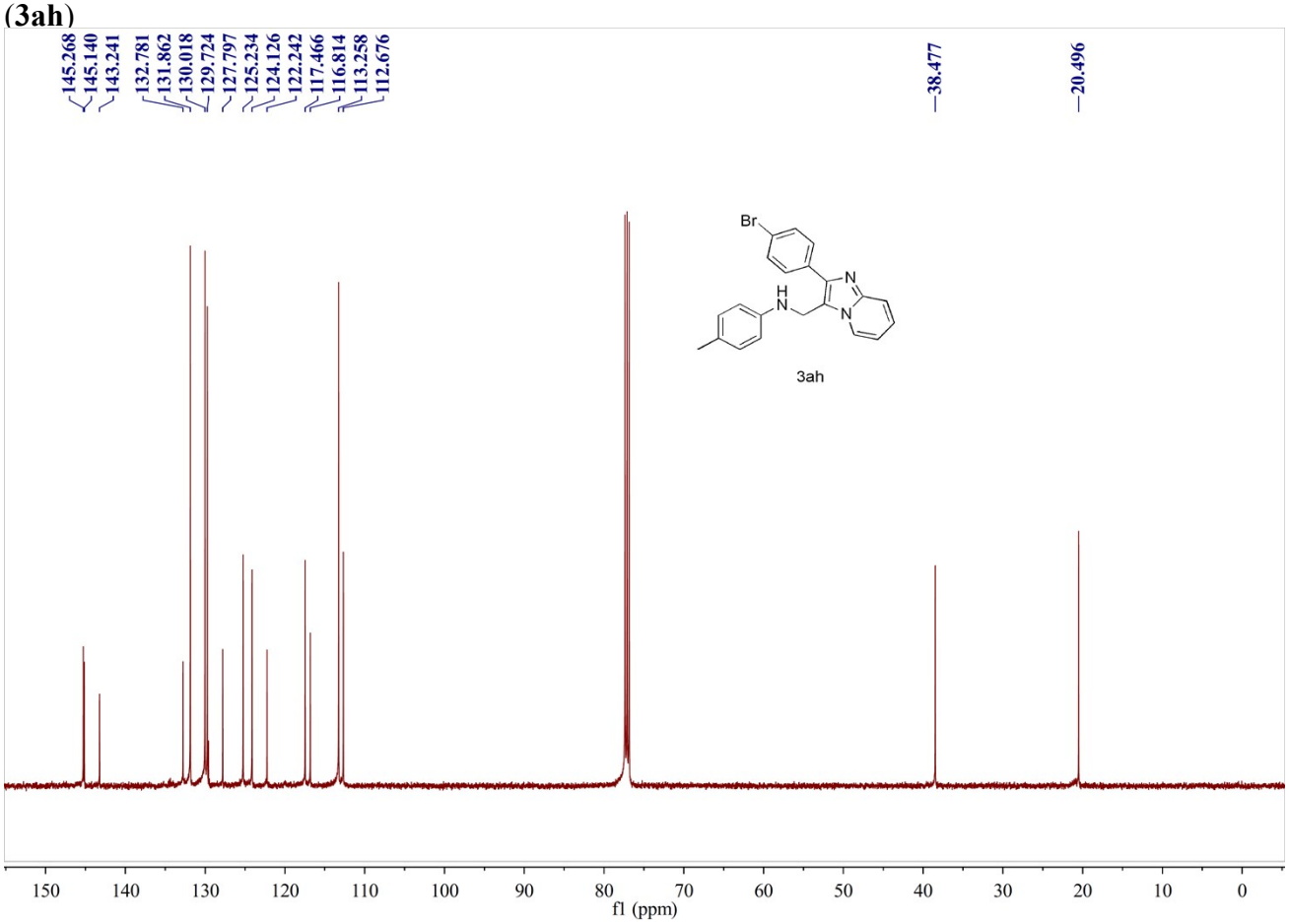
^{13}C NMR Spectra of *N*-((2-(4-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ag**)



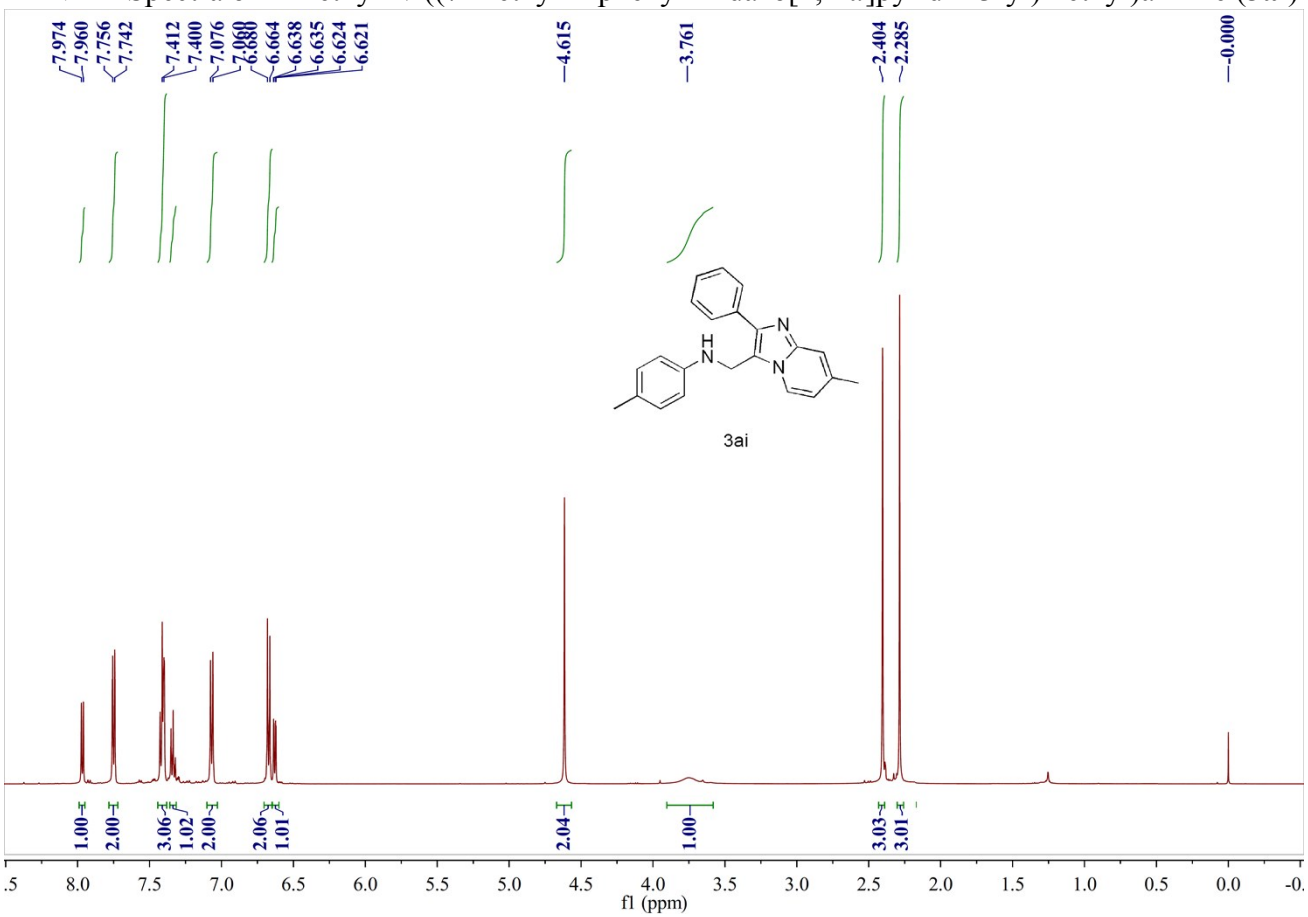
^{1}H NMR Spectra of *N*-((2-(4-bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline(**3ah**)



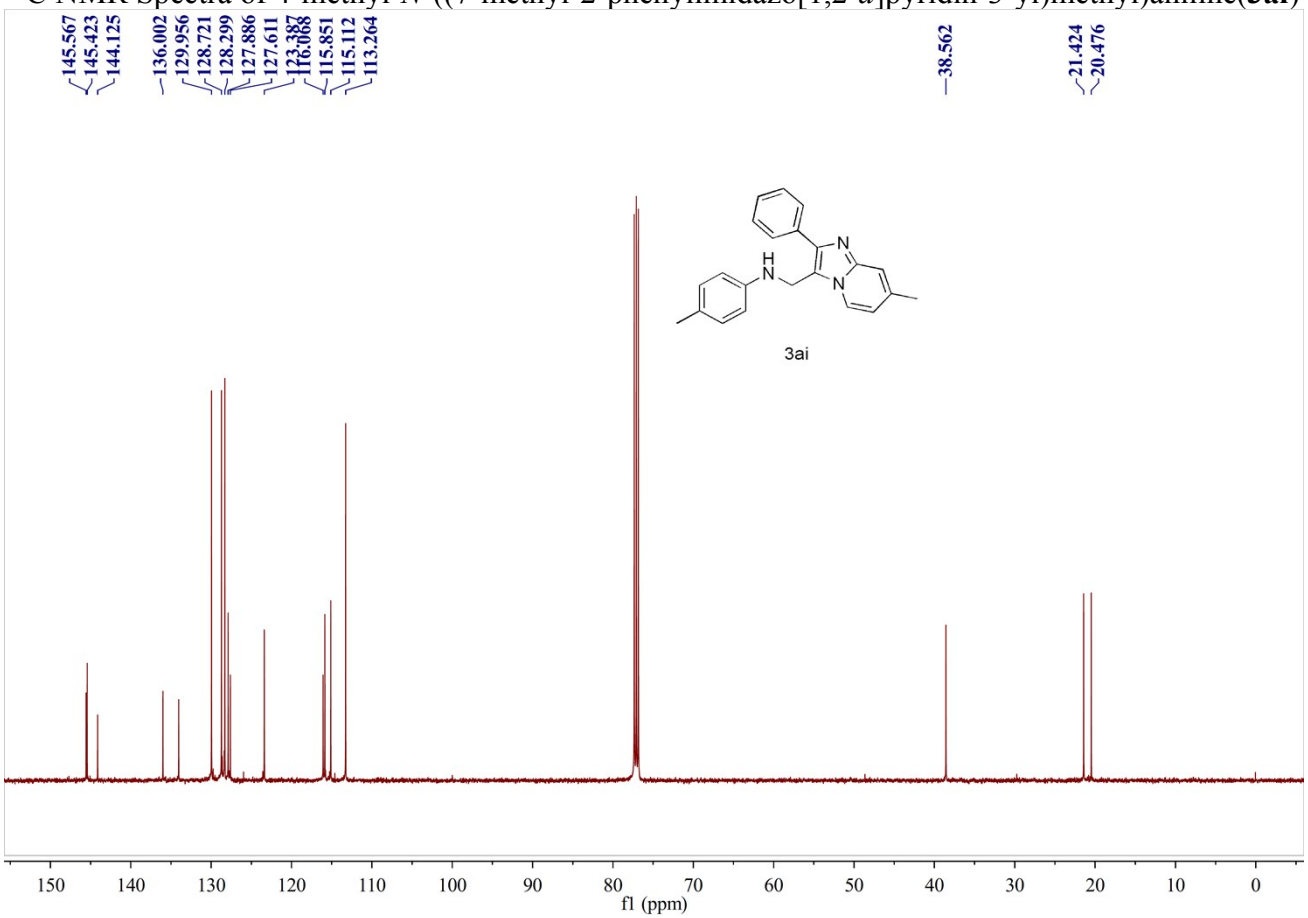
^{13}C NMR Spectra of *N*-((2-(4-bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ah**)



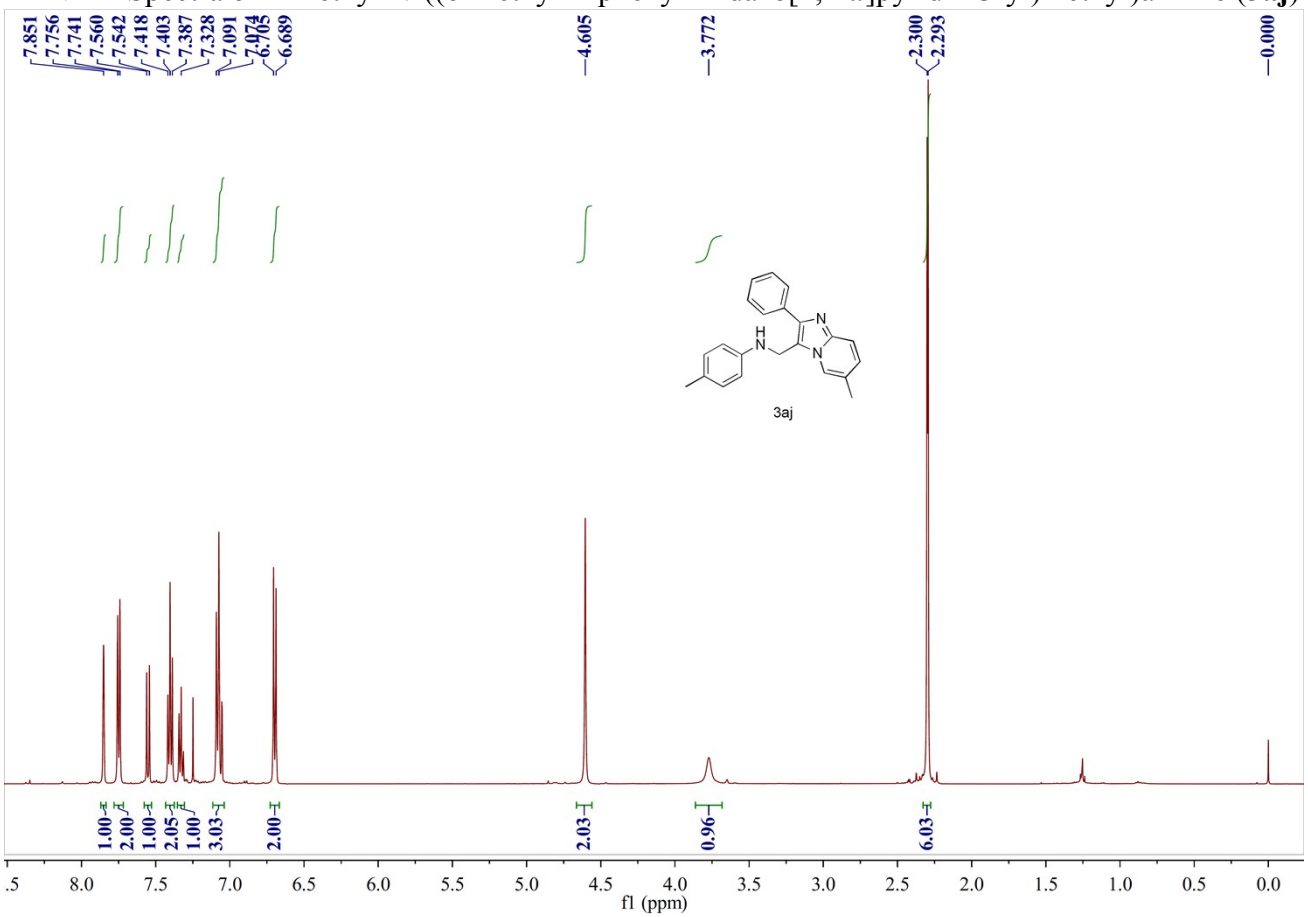
^{1}H NMR Spectra of 4-methyl-*N*-((7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3ai**)



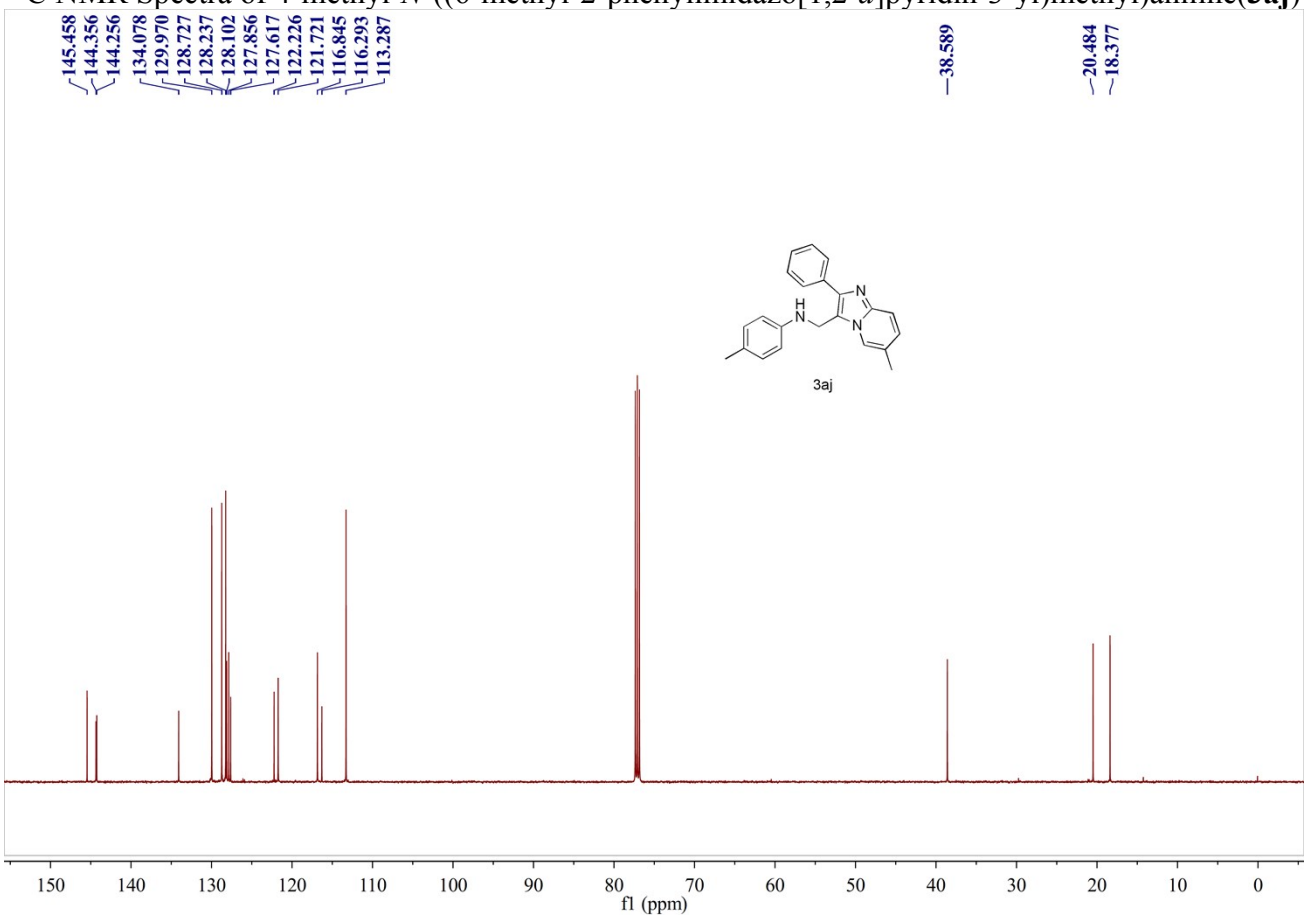
^{13}C NMR Spectra of 4-methyl-*N*-((7-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline(**3ai**)



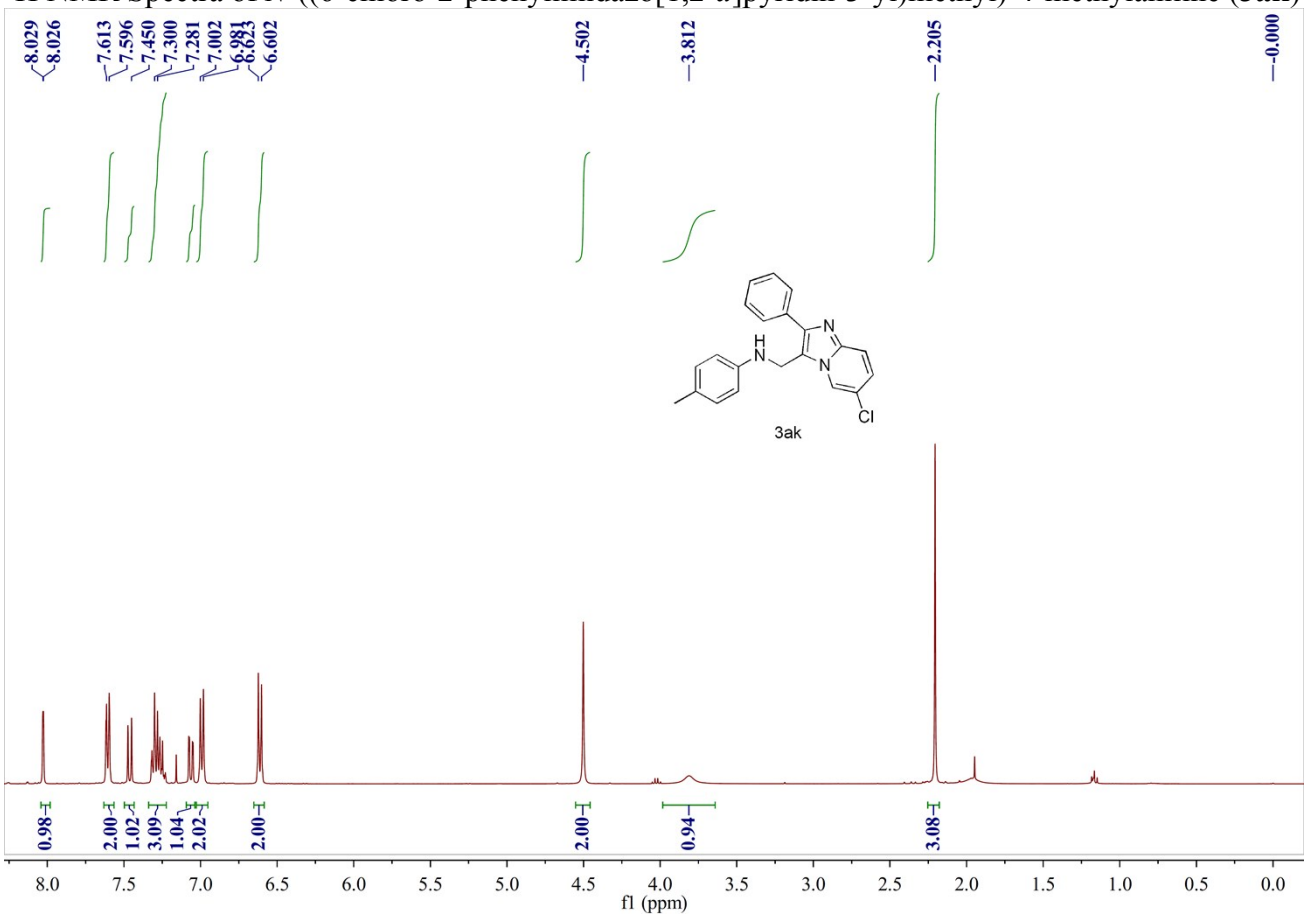
^{1}H NMR Spectra of 4-methyl-*N*-((6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (**3aj**)



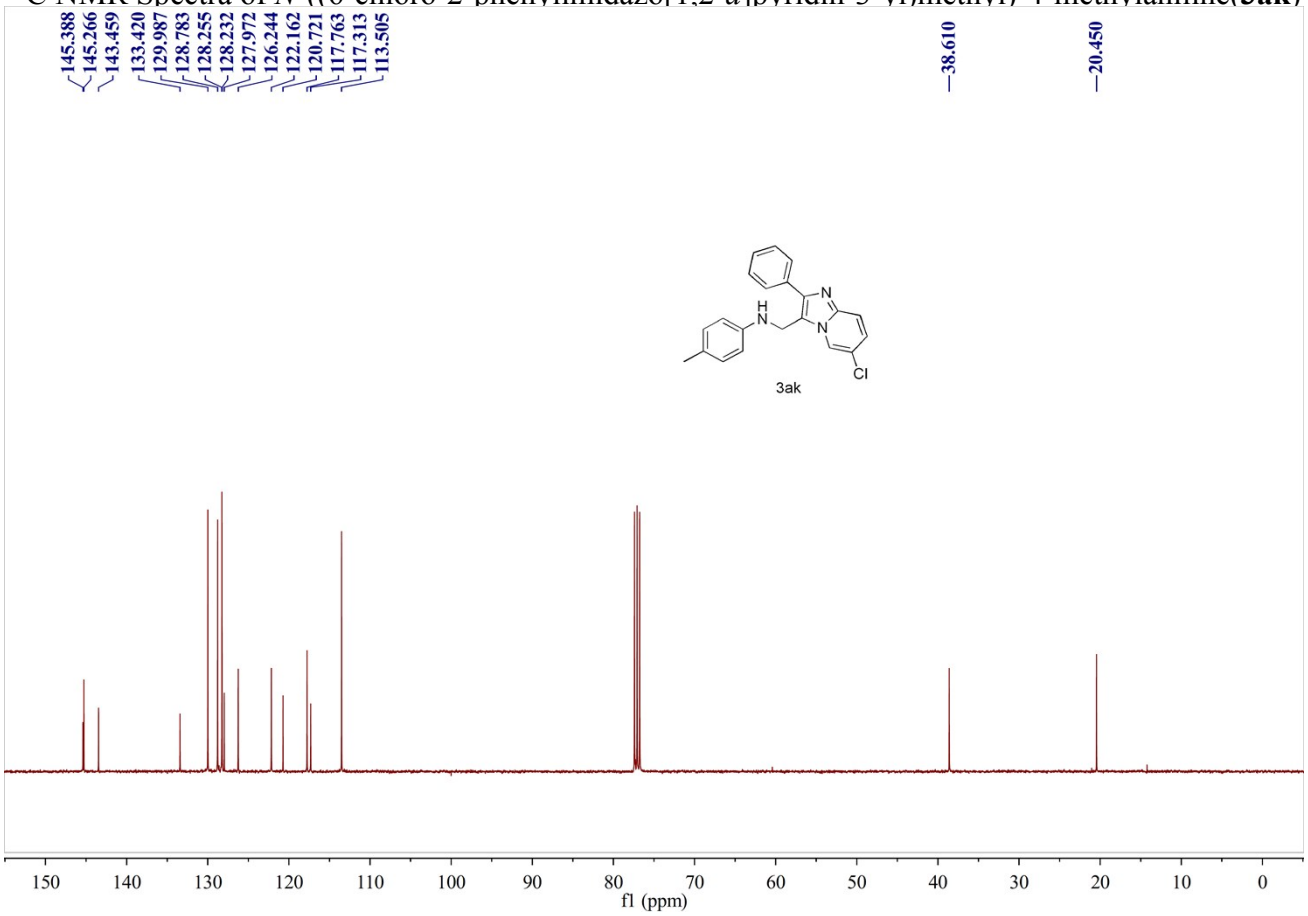
^{13}C NMR Spectra of 4-methyl-*N*-((6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline(**3aj**)



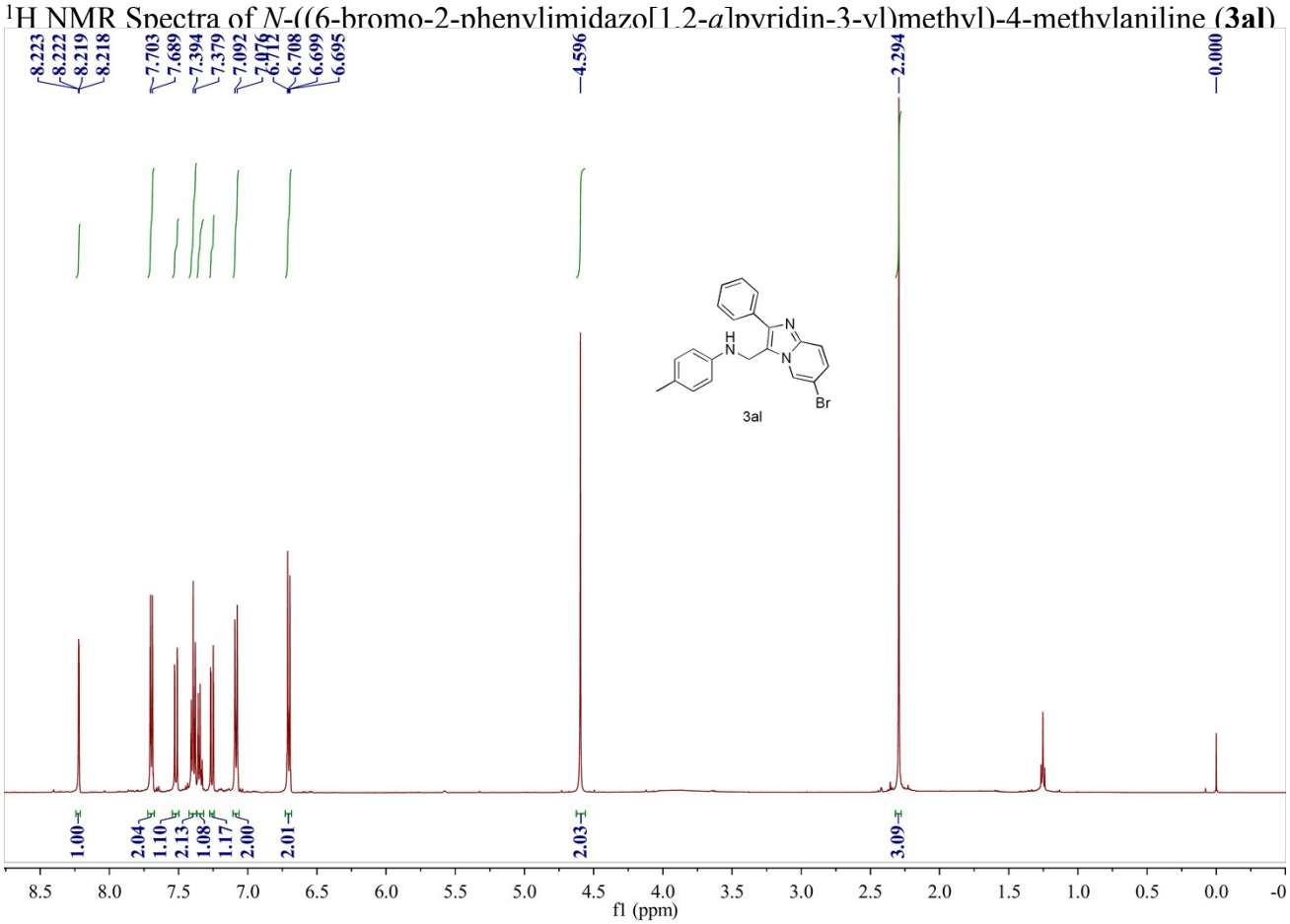
^{1}H NMR Spectra of *N*-((6-chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3ak**)



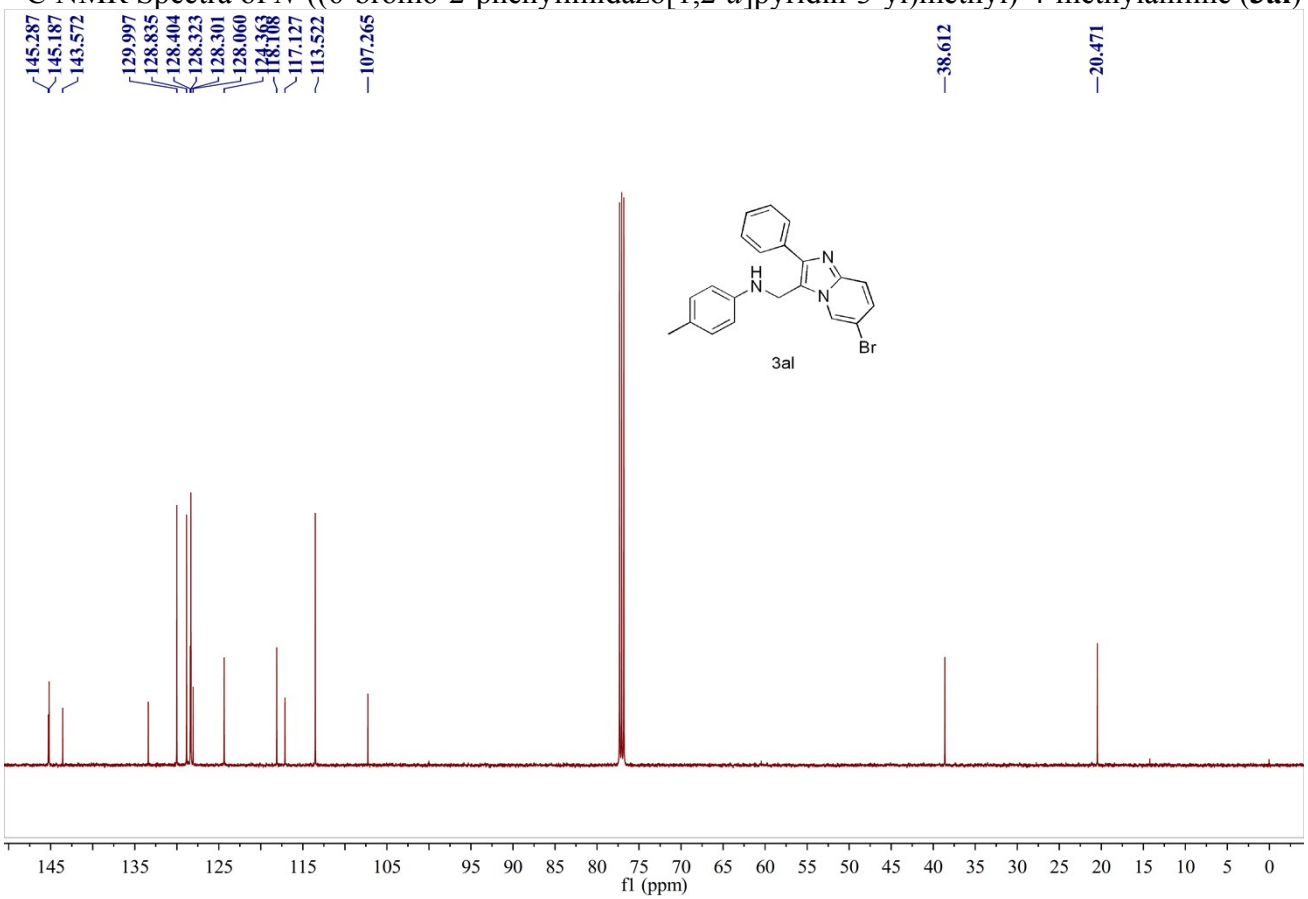
^{13}C NMR Spectra of *N*-((6-chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline(**3ak**)



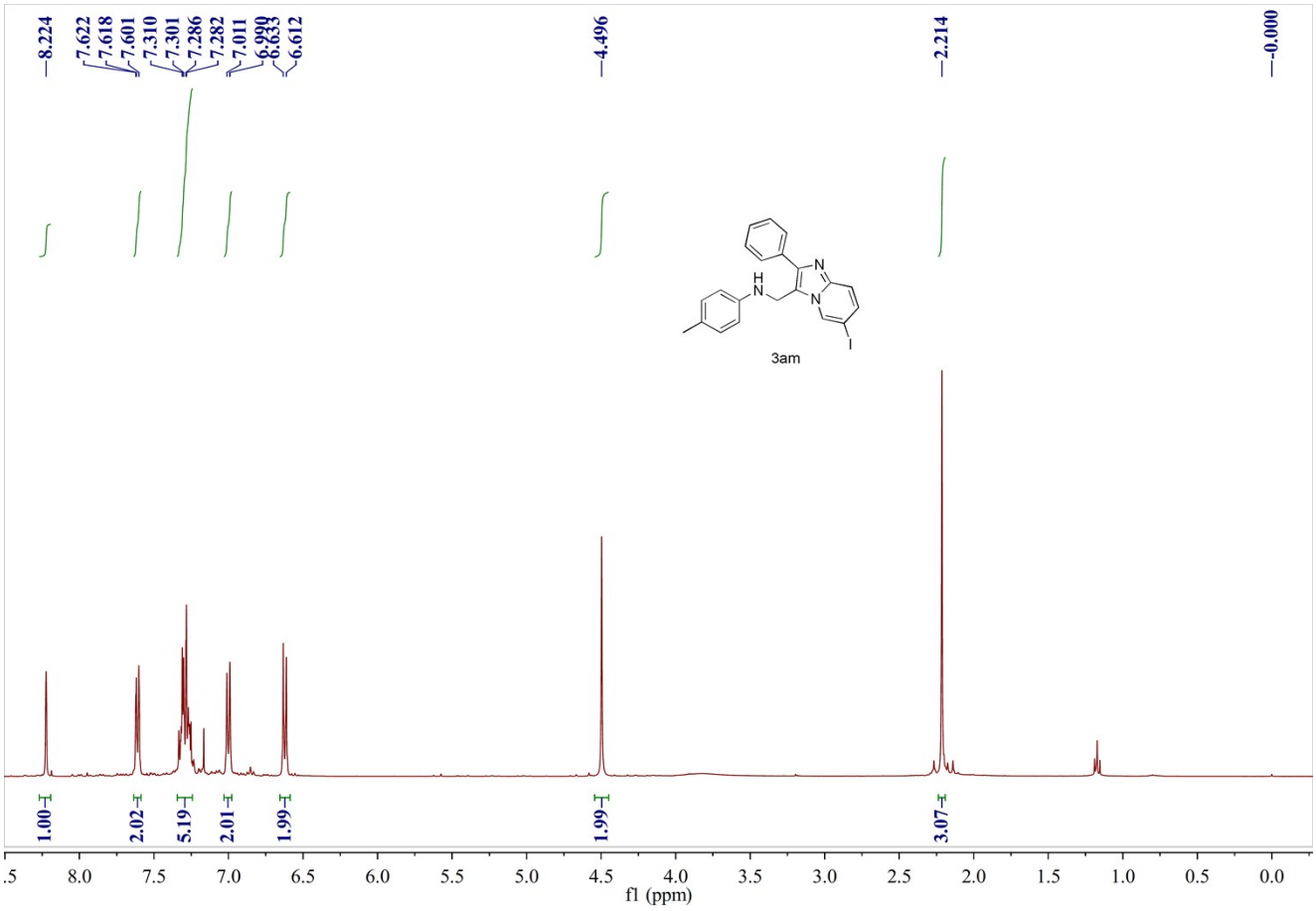
^{1}H NMR Spectra of *N*-((6-bromo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3al**)



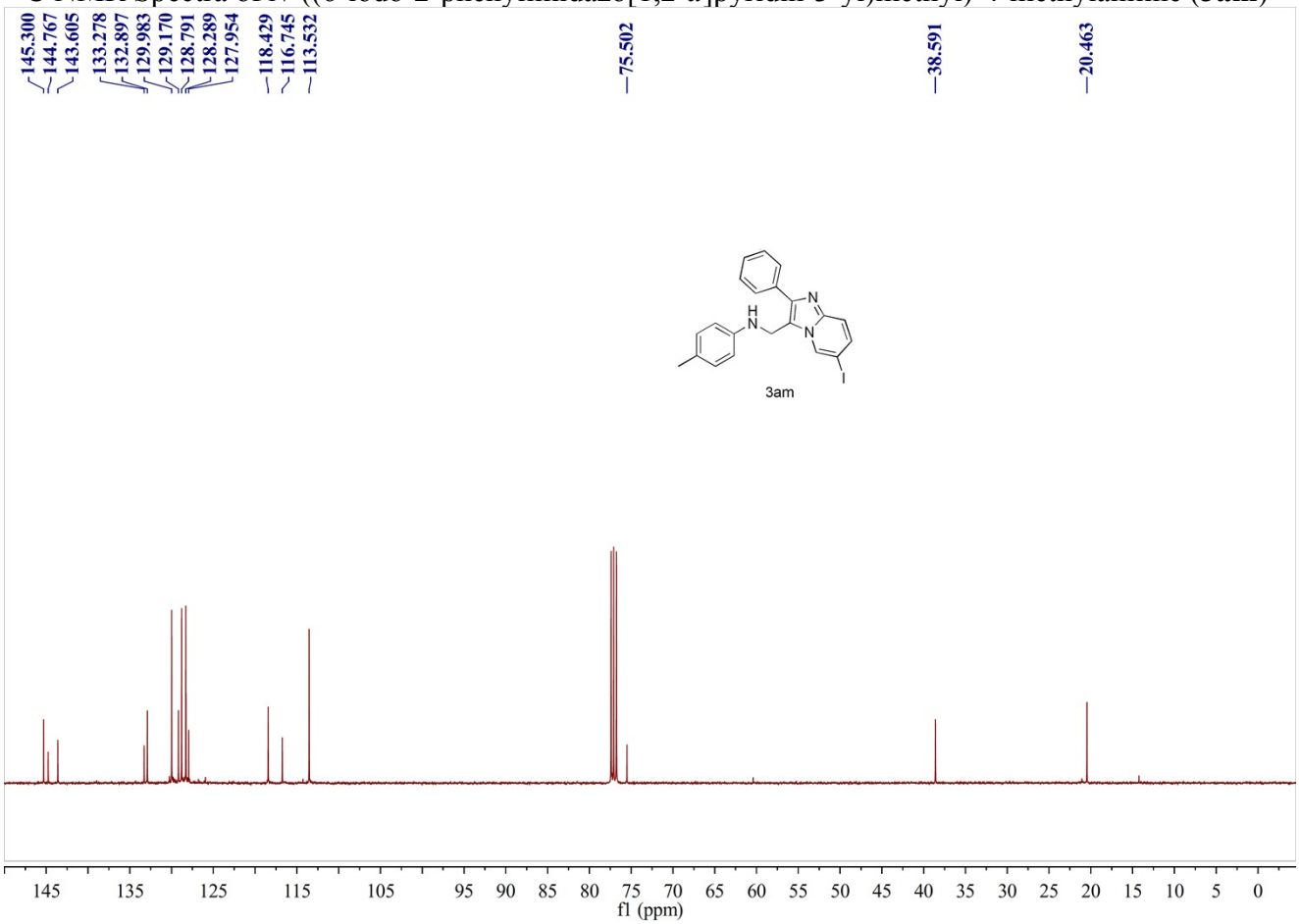
^{13}C NMR Spectra of *N*-((6-bromo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3al**)



^{1}H NMR Spectra of *N*-((6-iodo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3am**)

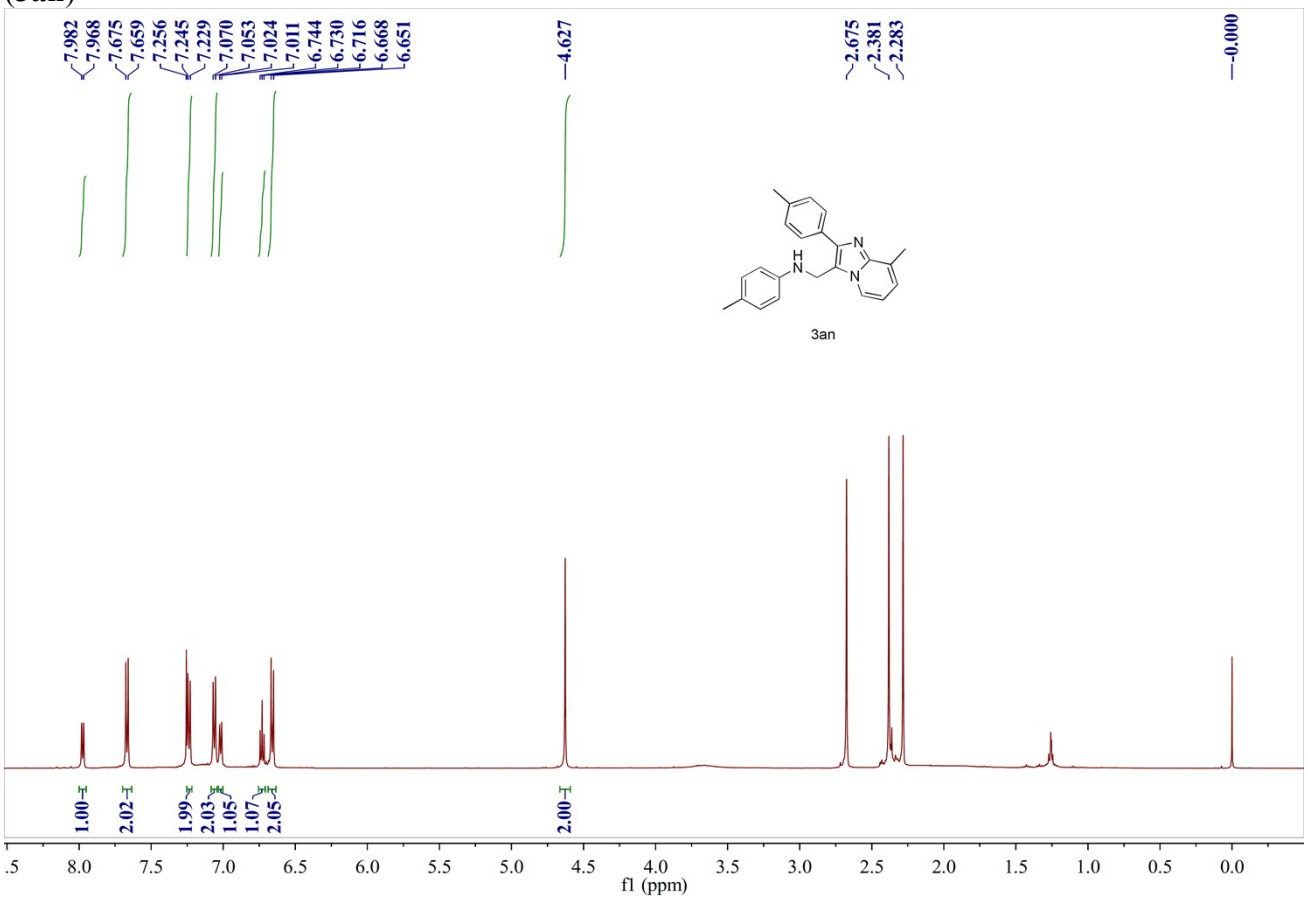


^{13}C NMR Spectra of *N*-((6-iodo-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methylaniline (**3am**)



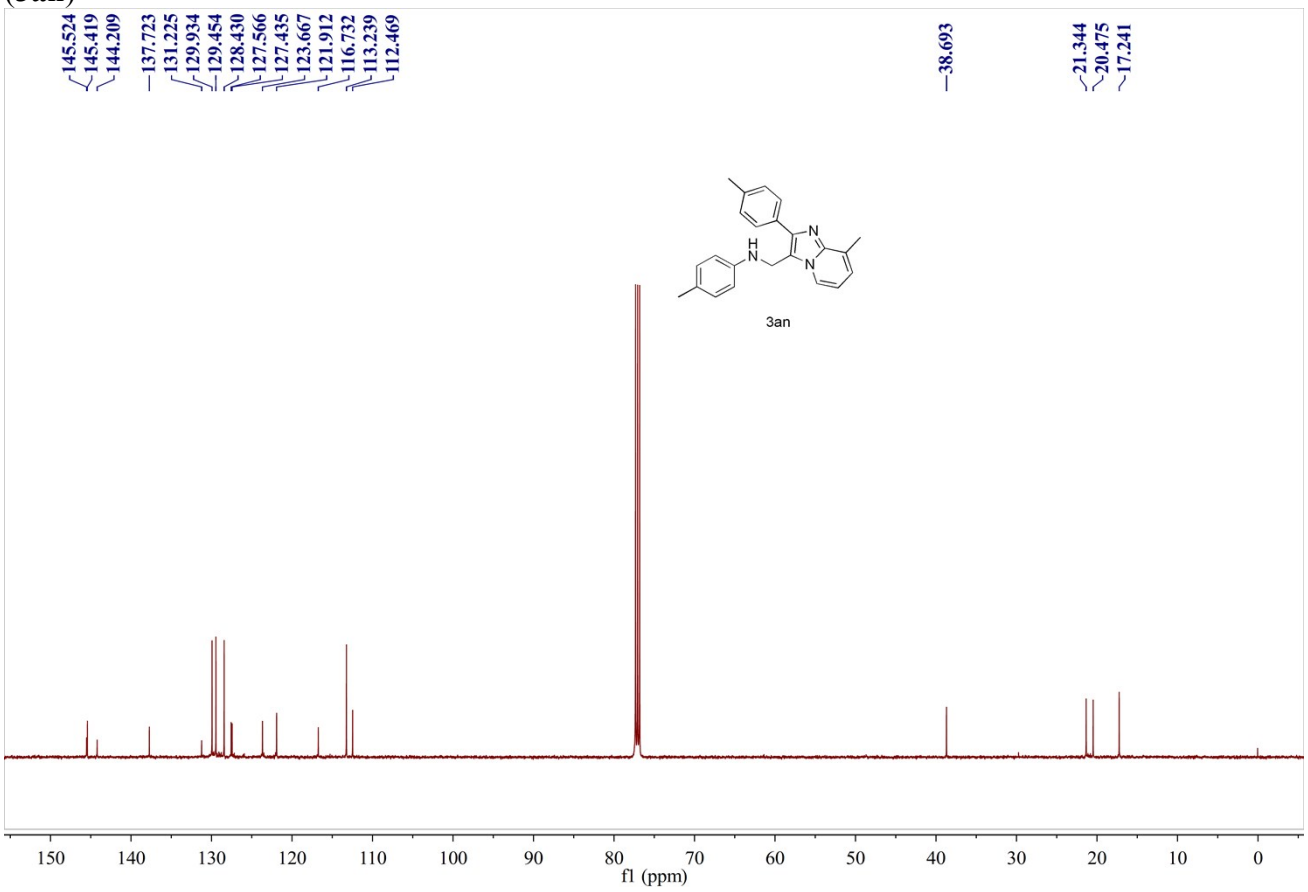
^{1}H NMR Spectra of 4-methyl-*N*-((8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline

(**3an**)



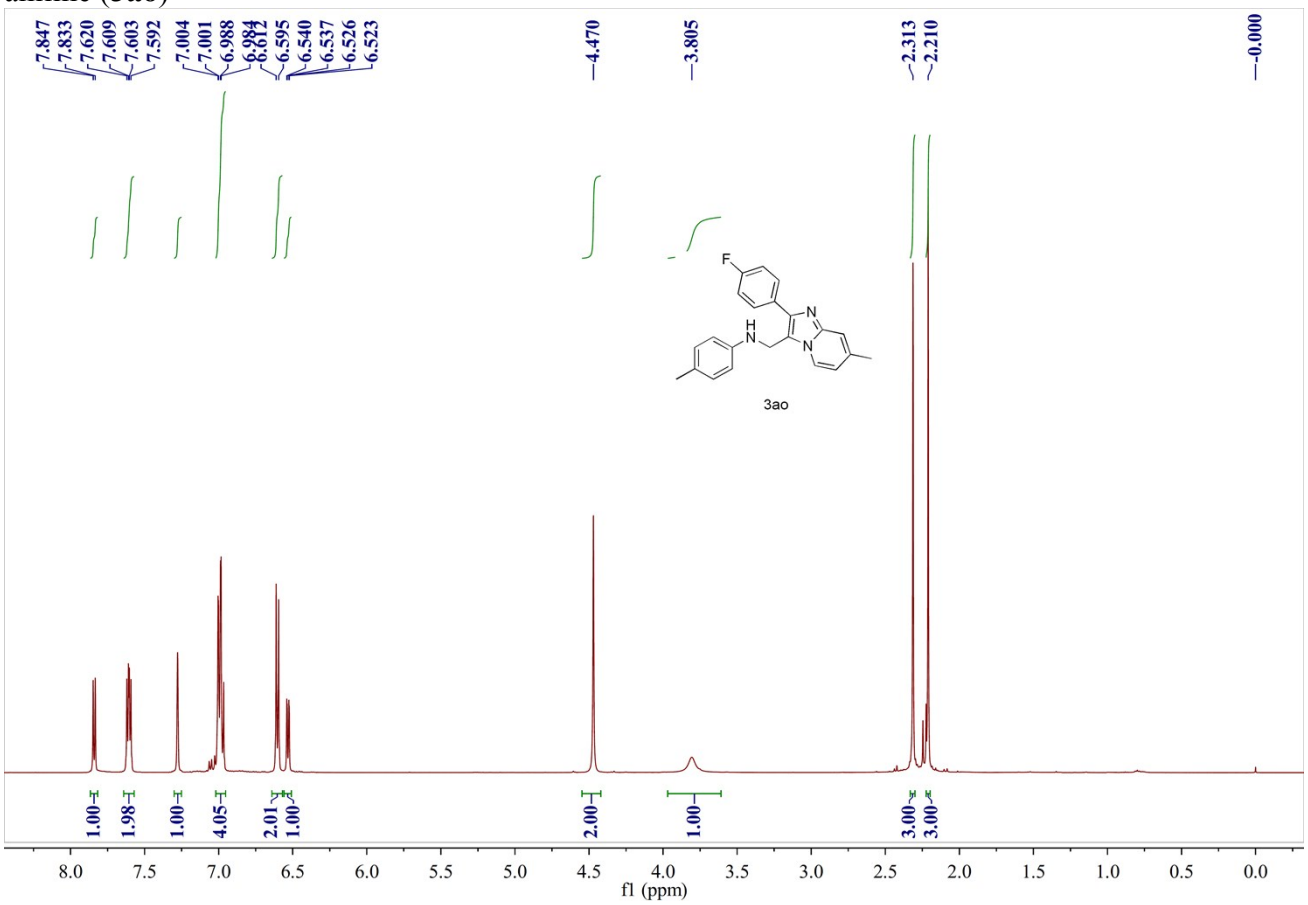
^{13}C NMR Spectra of 4-methyl-*N*-((8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)aniline

(**3an**)

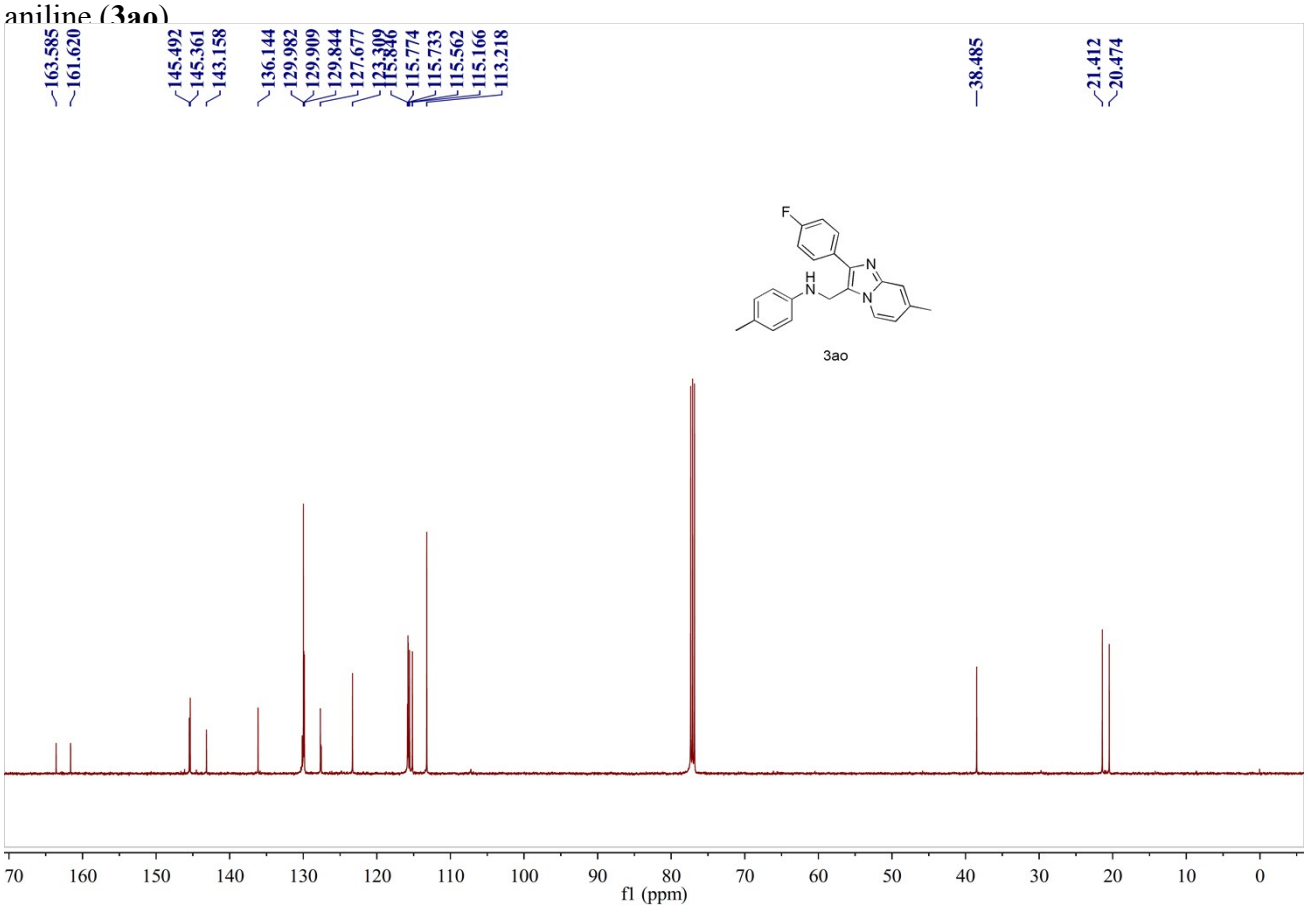


^{1}H NMR Spectra of *N*-((2-(4-fluorophenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-

aniline (**3ao**)

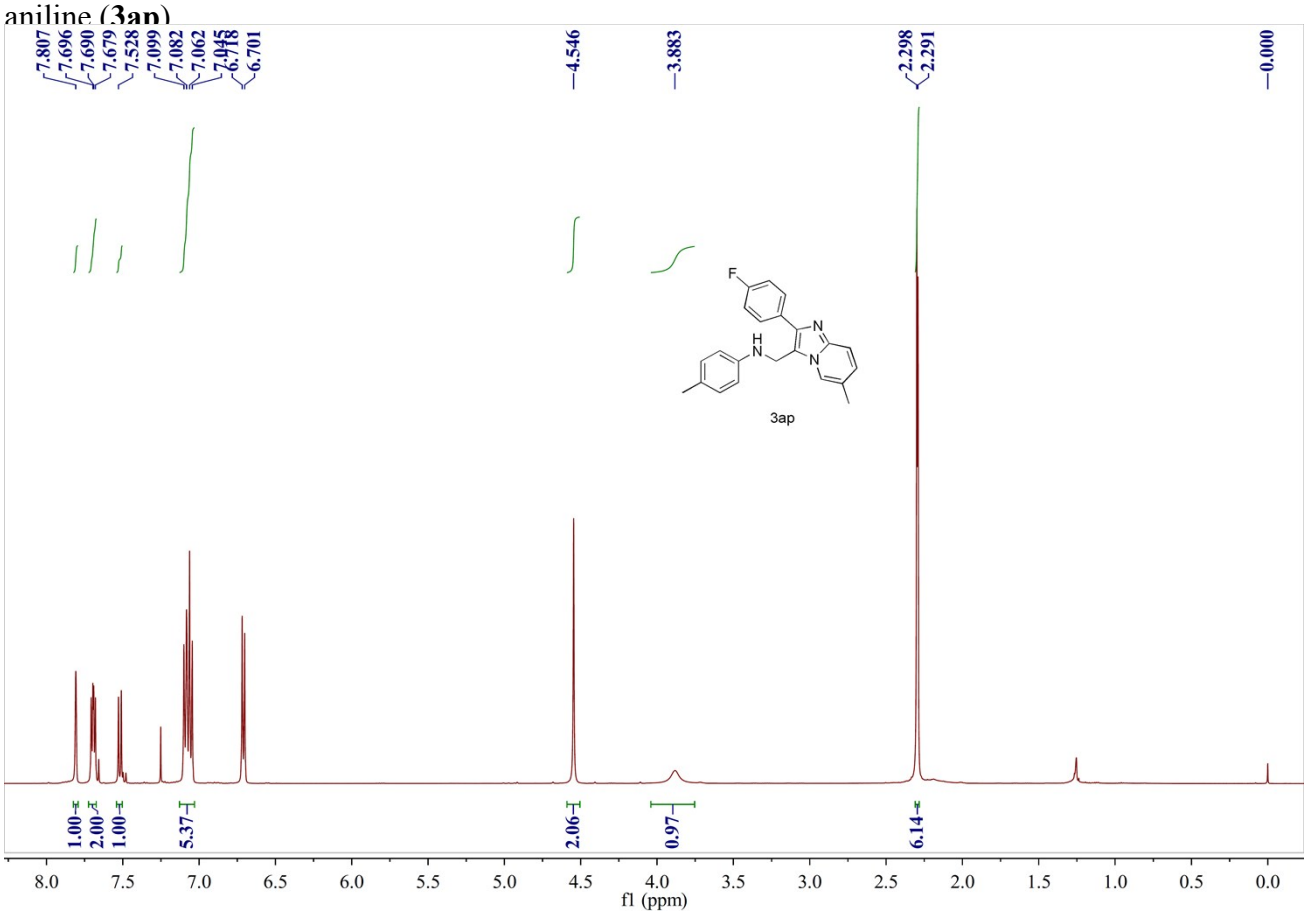


^{13}C NMR Spectra of *N*-((2-(4-fluorophenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-aniline (**3ao**)

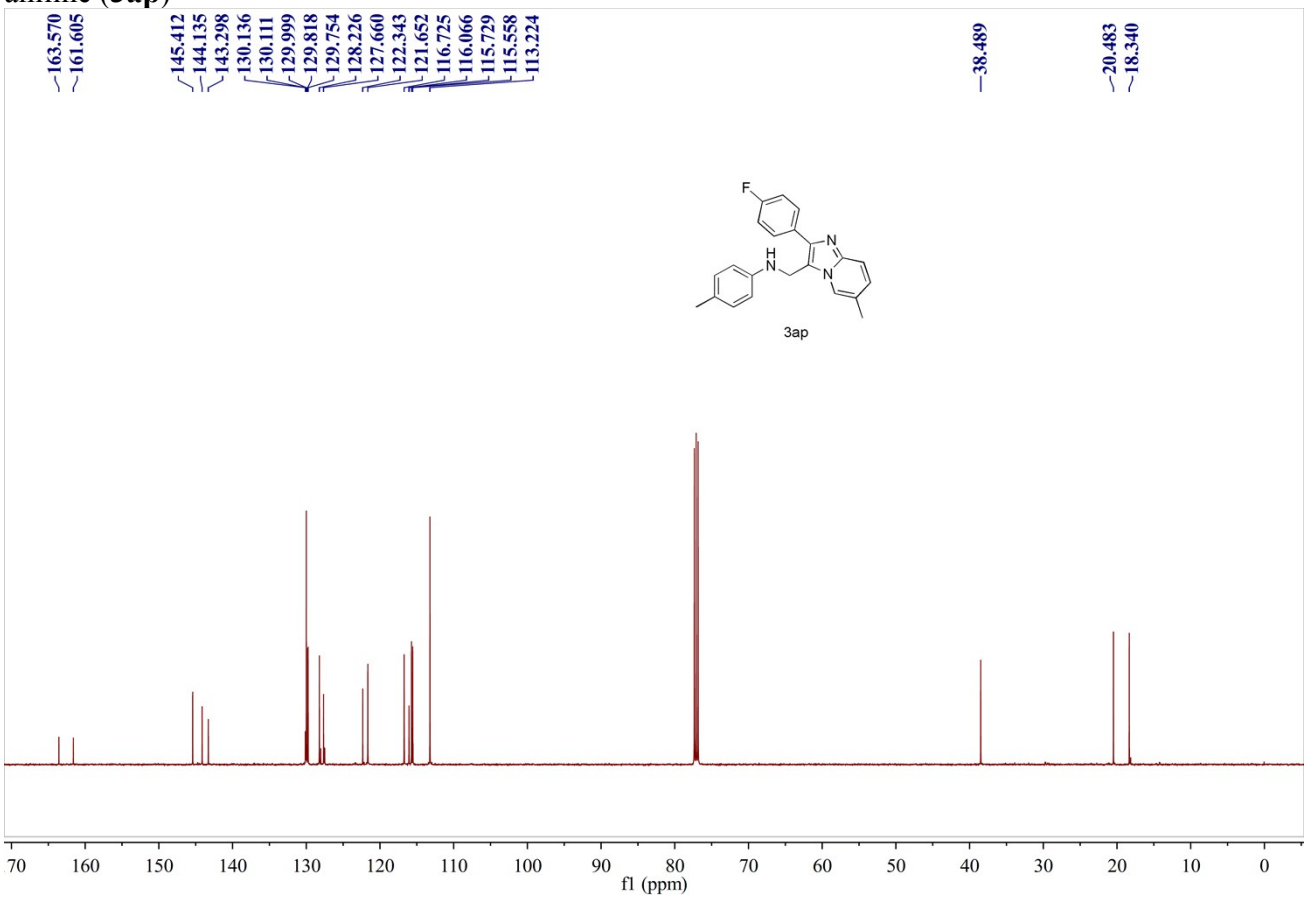


^{1}H NMR Spectra of *N*-((2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-

aniline (**3ap**)

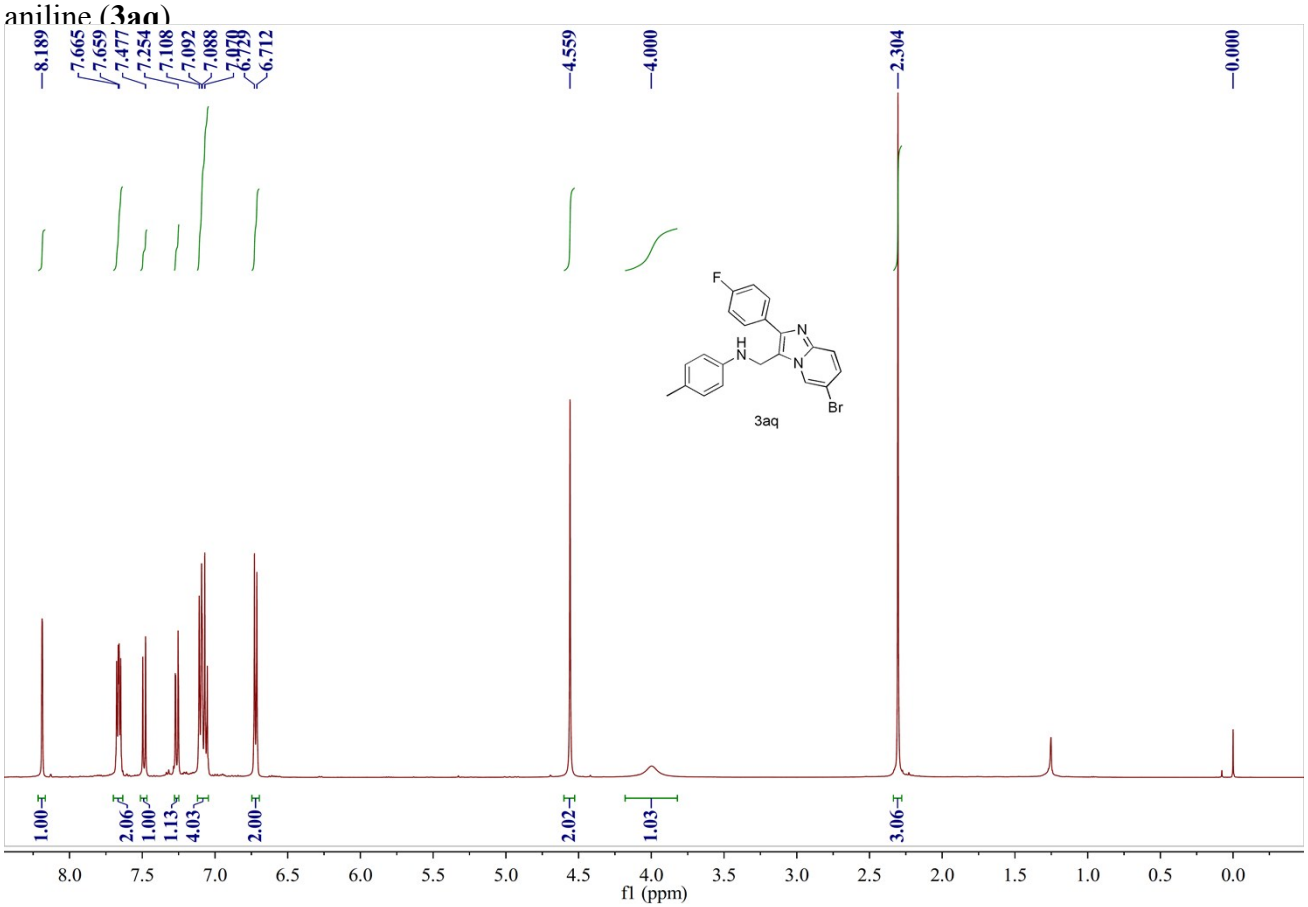


^{13}C NMR Spectra of *N*-((2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-aniline (**3ap**)

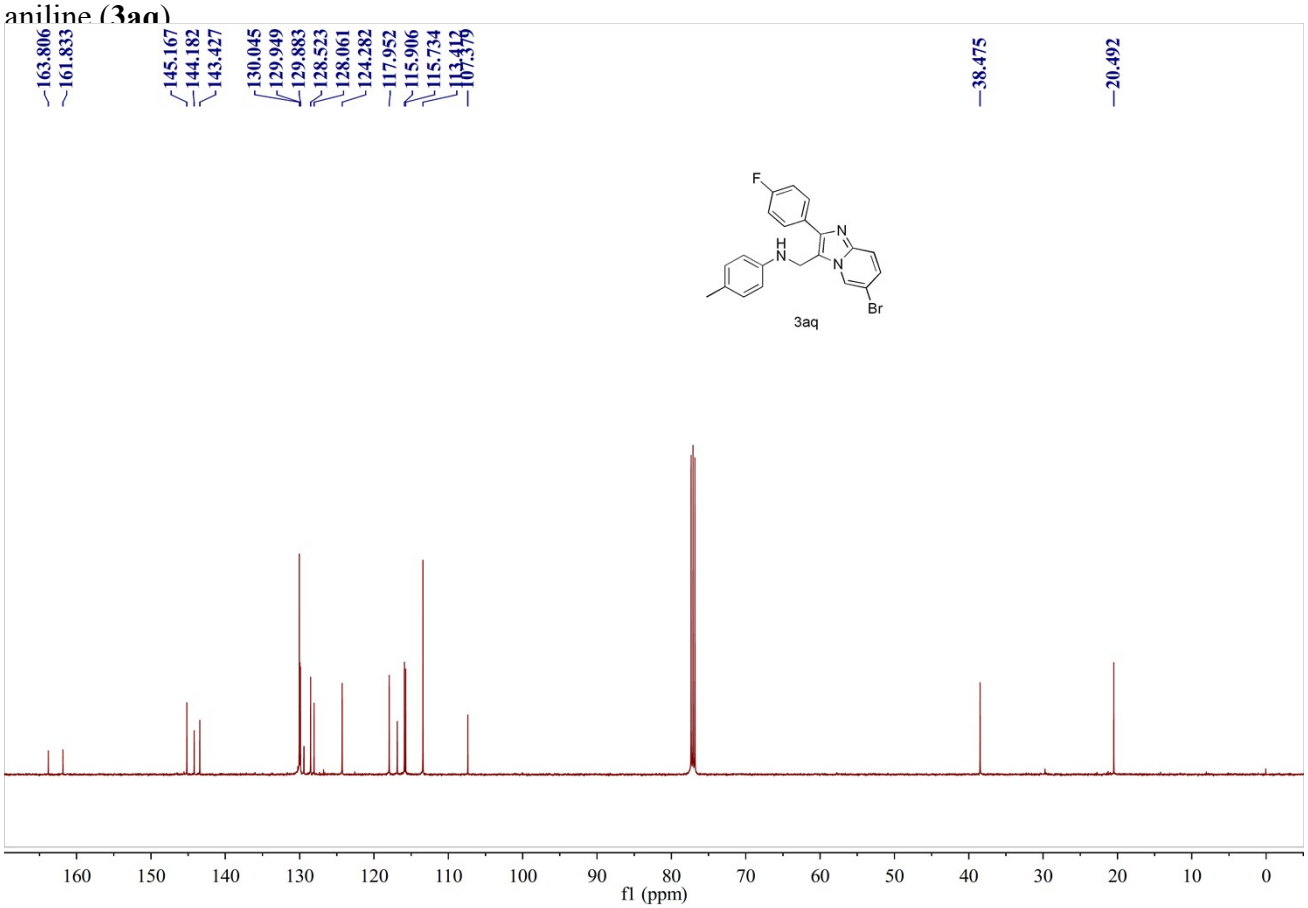


^{1}H NMR Spectra of *N*-((6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-

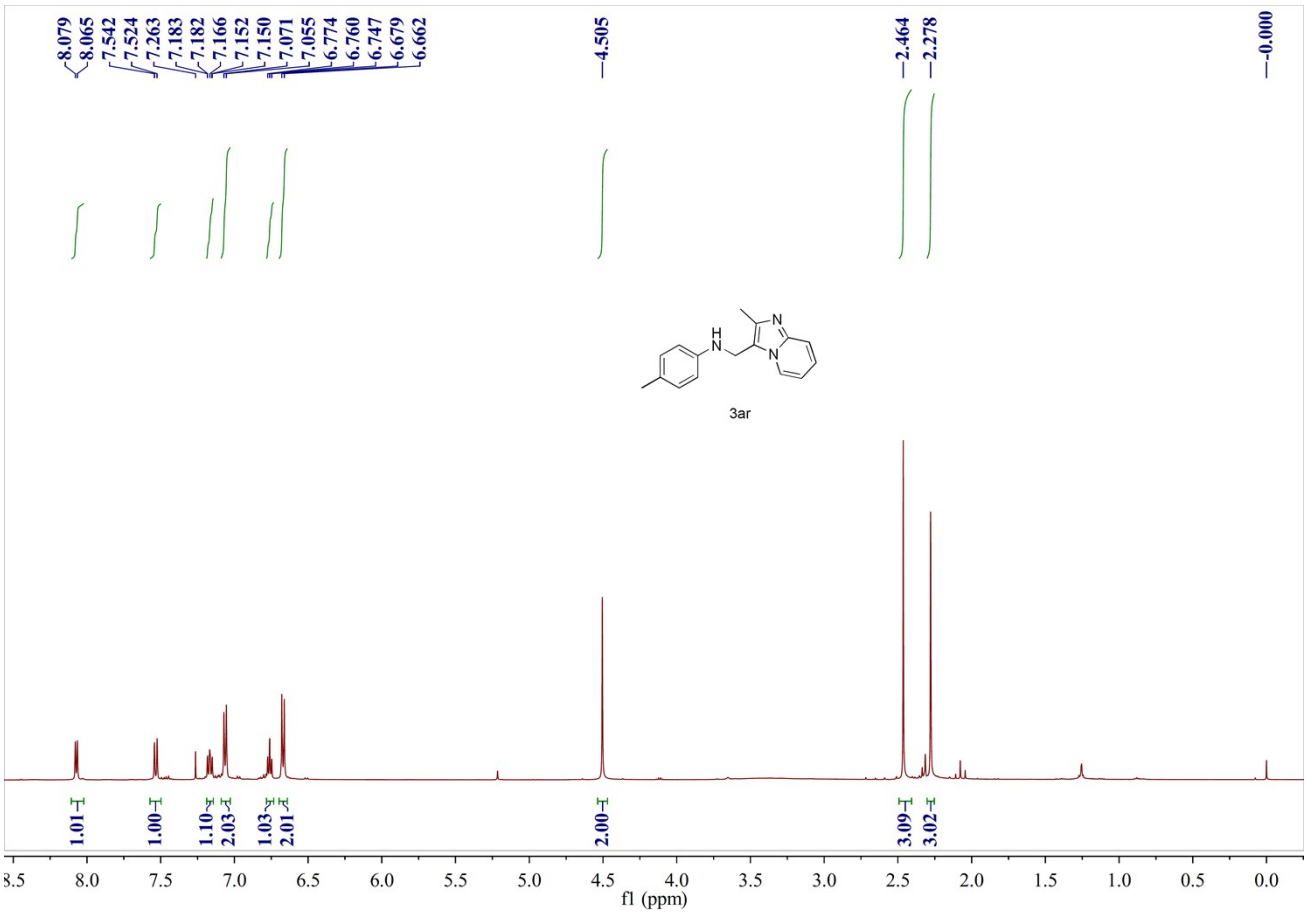
aniline (**3aq**)



^{13}C NMR Spectra of *N*-((6-bromo-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-4-methyl-aniline (**3aq**)



^{1}H NMR Spectra of 4-methyl-*N*-((2-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline(**3ar**)



^{13}C NMR Spectra of 4-methyl-*N*-((2-methylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline(**3ar**)