N-Aroyloxycarbamates as switchable nitrogen and oxygen precusor: Ir/Cu controlled divergent C–H functionalizaion of heteroarenes

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Supporting Information

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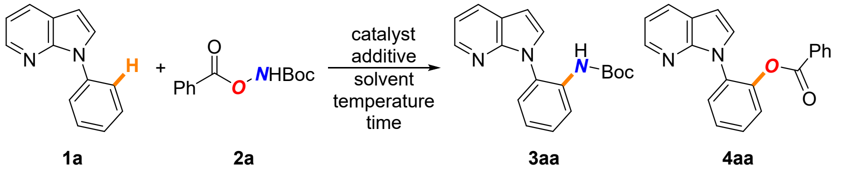
1. General Information

All purchased reagents were used without further purification unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. ^{1}H nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. ^{13}C NMR data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$.Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer. **1a–1m** were prepared according to literature methods[S1], **2a** and **2f–2t** were prepared according to literature methods[S2] and **2u** was prepared according to literature methods[S3].

2 Full Table of Reaction Optimization

Table S1 Identification of reaction conditions for the transformation between 7-azaindole and *N*-benzyloxycarbamate



Entry	Catalyst	Ligand	Additives	Temperature (ºC)	Solvent	Yield of **3aa** (%)[a]	Yield of **4aa** (%)[a]
1	$[IrCp^*Cl_2]_2$	–	$AgNTf_2$ (10 mol%)	rt	DCE	70	–
2	$[IrCp^*Cl_2]_2$	–	$AgNTf_2$ (10 mol%)	rt	$BMIMPF_6$	73	–
3	$[IrCp^*Cl_2]_2$	–	$AgNTf_2$ (10 mol%)	rt	$BMIMNTf_2$	75	–
4	$[IrCp^*Cl_2]_2$	–	$AgNTf_2$ (10 mol%)	rt	$BMIMBF_4$	82 (89[b])	–
5	$[IrCp^*Cl_2]_2$	–	$AgSbF_6$ (10 mol%)	rt	$BMIMBF_4$	83[b]	–
6	$[IrCp^*Cl_2]_2$	–	AgOAc (10 mol%)	rt	$BMIMBF_4$	80[b]	–
7	$[IrCp^*Cl_2]_2$	–	AgOTf (10 mol%)	rt	$BMIMBF_4$	98[b]	–
8	$[Cp^*RhCl_2]_2$ (5 mol%)	–	AgOTf (10 mol%)	rt	$BMIMBF_4$	25	–
9	Fe(TPP)Cl (10 mol%)	–	K_2CO_3	100	toluene	–	–
10	$Zn(OTf)_2$ (10 mol%)	–	–	100	toluene	–	–
11	$Ni(acac)_2$ (10 mol%)	$MePPh_3$ (20 mol%)	–	100	toluene	–	–
12	$Pd(OAc)_2$ (20 mol%)	–	–	100	toluene	–	–
13	$Cu(OAc)_2$ (20 mol%)	–	–	100	toluene	–	–
14	CuTc	–	–	100	toluene	–	trace
15	$Cu(OAc)_2$	–	–	100	toluene	–	18
16	$Cu(OAc)_2$	2,6-lutidine	–	100	toluene	–	32
17	$Cu(OTf)_2$	2,6-lutidine	–	100	toluene	–	26
18	CuCN	2,6-lutidine	–	100	toluene	–	–

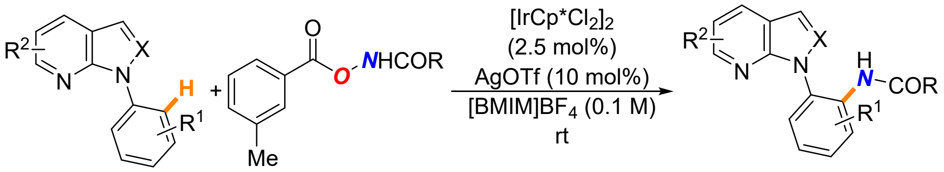
19	CuI	2,6-lutidine	–	100	toluene	–	–
20	CuCl	2,6-lutidine	–	100	toluene	–	–
21	CuBr·SMe	2,6-lutidine	–	100	toluene	–	–
22	Cu_2O	2,6-lutidine	–	100	toluene	–	–
23	$Cu(CH_3CN)_4BF_4$	2,6-lutidine	–	100	toluene	–	47
24	$Cu(CH_3CN)_4PF_6$	2,6-lutidine	–	100	toluene	–	42
25	$Cu(CH_3CN)_4BF_4$	2-aminopyrin	–	100	toluene	–	36
26	$Cu(CH_3CN)_4BF_4$	2-methyl-4-aminopyridine	–	100	toluene	–	42
27	$Cu(CH_3CN)_4BF_4$	4,4’-di-*tert*-butyl-2,2'-bipyridine	–	100	toluene	–	trace
28	$Cu(CH_3CN)_4BF_4$	2-amino-trimethylpyridine	–	100	toluene	–	–
29	$Cu(CH_3CN)_4BF_4$	6-methyl-2pyridinitrile	–	100	toluene	–	47
30	$Cu(CH_3CN)_4BF_4$	2-fluoro-6-methylpyridine	–	100	toluene	–	57
31	$Cu(CH_3CN)_4BF_4$	DMAP	–	100	toluene	–	55
32	$Cu(CH_3CN)_4BF_4$	1,10-pnenanthroline	–	100	toluene	–	trace
33	$Cu(CH_3CN)_4BF_4$	2,9-dimethyl-1,10-pnenanthroline	–	100	toluene	–	–
34	$Cu(CH_3CN)_4BF_4$	–	–	100	toluene	–	55 (52[c])
35	$Cu(CH_3CN)_4BF_4$ (50 mol%)	–	–	100	toluene	–	44[d]
36	$Cu(CH_3CN)_4BF_4$	–	TFA	100	toluene	–	21[c]
37	$Cu(CH_3CN)_4BF_4$	–	TSoH·H_2O	100	toluene	–	16[c]
38	$Cu(CH_3CN)_4BF_4$	–	DABCO	100	toluene	–	–
39	$Cu(CH_3CN)_4BF_4$	–	TMEDA	100	toluene	–	–
40	$Cu(CH_3CN)_4BF_4$	–	TBHP	100	toluene	–	50[c]
41	$Cu(CH_3CN)_4BF_4$	–	DTBP	100	toluene	–	58[c]
42	$Cu(CH_3CN)_4BF_4$	–	–	100	toluene	–	52[c]
43	$Cu(CH_3CN)_4BF_4$	–	–	80	toluene	–	39[c]
44	$Cu(CH_3CN)_4BF_4$	–	–	120	toluene	–	70[c]
45	$Cu(CH_3CN)_4BF_4$	–	–	140	toluene	–	71[c]
46	$Cu(CH_3CN)_4BF_4$	–	–	120	CH_3CN	–	–
47	$Cu(CH_3CN)_4BF_4$	–	–	120	THF	–	–
48	$Cu(CH_3CN)_4BF_4$	–	–	120	dioxane	–	–

49	$Cu(CH_3CN)_4BF_4$	–	–	120	DFM	–	–
50	$Cu(CH_3CN)_4BF_4$	–	–	120	NMP	–	–
51	$Cu(CH_3CN)_4BF_4$	–	–	120	EtOH	–	–
52	$Cu(CH_3CN)_4BF_4$	–	–	120	DCE	–	54^c
53	$Cu(CH_3CN)_4BF_4$	–	–	120	DCB	–	83^c
54	$Cu(CH_3CN)_4BF_4$	–	–	120	PhCl	–	85^c
55	$Cu(CH_3CN)_4BF_4$	–	–	120	$PhCF_3$	–	81^c
56	$Cu(CH_3CN)_4BF_4$	–	–	120	xylene	–	75^c

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.12 mmol), additives (1.0 equiv.), ligand (1.0 equiv.) and Iridium catalyst (2.5 mol%) or copper salt (1.0 equiv.) in solvent (1.0 mL) were stirred at indicated temperature for 1−12 h under air, isolated yield reported. [b] *m*-Tolueneoxy carbamate was used.[c] 60 mol% copper salt was used. [d] 50 mol% copper salt was used.

3 Experimental Details for Ir(III) Catalyzed Amidation Reactions

3.1 General Procedure for the Catalytic Amidation (GP A)



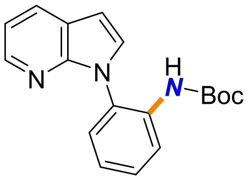
1 **2** **3aa–3ma'**, **3af–3ag**

To an oven dried Schlenk tube (10 mL) was added *N*-aryl-7-azaindole **1** (0.1 mmol), hydroxylamines **2** (1.2 equiv.), $[IrCp^*Cl_2]_2$ (2 mg, 2.5 mol%), AgOTf (2.6 mg, 10 mol%) in 1.0 mL of $[BMIM]BF_4$ under air, the reaction mixture was stirred at room temperature for 1-12 h. The crude reaction mixture was purified through column chromatography using hexane/ethyl acetate as eluent to afford aryl amines**.**

3.2 Studies on Reuse of Catalytic System

The feasibility of recycling the catalyst system was studied under the optimized reaction condition according to **GP A**. After completion of the reaction, the product was separated by extraction with diethyl ether. The upper layer of diethyl ether contains a product mixture directly used for purification. The remains were subsequently subjected to vacuum to remove the rest of solvents before it was reused in next catalytic run. Purification by flash column chromatography to afford the pure product **3aa** (30.2 mg, 98%), (28.4 mg, 92%), and (27.8 mg, 90%) in three cycles, respectively.

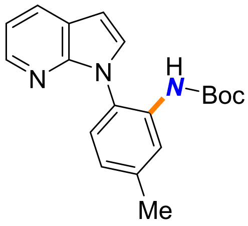
3.3 Characterization Data of the Amidation Products



3aa

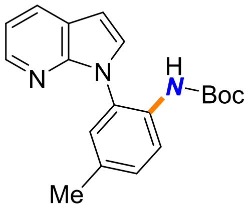
tert*-Butyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3aa** was prepared according to **GP A**, The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (30.2 mg, 98%). **R*f= 0.63; **m.p.** = 128–129 °C; **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): δ = 8.47 (s, 1H), 8.26 (d, *J* = 4.7 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 9.4, 5.7

Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 1.26 (s, 9H) ppm; **^{13}C NMR** (101 MHz, DMSO): *δ* = 153.4, 147.8, 143.3, 134.0, 132.0, 130.5, 129.6, 128.6, 128.2, 126.3, 125.6, 121.2, 117.0, 102.1, 79.5, 28.3 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3083, 1730, 1603, 1503, 1275, 1064, 709; **HRMS** (ESI) m/z: calculated for $C_{18}H_{19}N_3O_2$ [M+H]$^+$ 310.1550, found 310.1541.



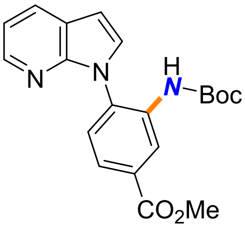
3ba

tert*-Butyl (5-methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ba** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (29.4 mg, 91%). **R*$_f$ = 0.56; **m.p.** = 135–136 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): *δ* = 8.34 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.00 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.90 (s, 1H), 7.41 (s, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.98 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 2.42 (s, 3H), 1.40 (s, 9H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): *δ* = 153.2, 148.2, 143.7, 138.7, 133.8, 129.7, 129.6, 127.3, 126.7, 124.9, 123.7, 121.2, 116.6, 102.2, 80.3, 28.2, 21.4 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3082, 2926, 1722, 1603, 1485, 1393, 1229, 1064, 717; **HRMS** (ESI) m/z: calculated for $C_{19}H_{22}N_3O_2$ [M+H]$^+$ 324.1707, found 324.1705.



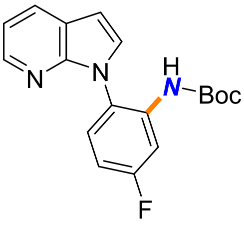
3ca

tert*-Butyl (4-methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ca** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (29.1 mg, 90%). **R*$_f$ = 0.53; **^{1}H NMR** (400 MHz, CDCl$_3$): *δ* = 8.40 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.05 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.20 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.10 (d, *J* = 2.1 Hz, 1H), 6.72 (d, *J* = 3.6 Hz, 1H), 2.40 (s, 3H), 1.44 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 153.5, 148.1, 143.7, 134.3, 131.4, 129.7, 129.5, 129.2, 128.0, 124.0, 121.3, 126.7, 116.7, 102.3, 80.2, 28.3, 20.7 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3085, 2932, 1733, 1643, 1481, 1393, 1229, 1054, 717; **HRMS** (ESI) m/z: calculated for $C_{19}H_{22}N_3O_2$ [M+H]$^+$ 324.1707, found 324.1705.



3da

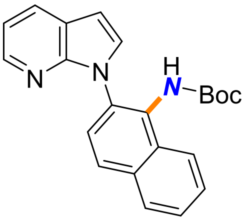
Methyl 3-((*tert*-butoxycarbonyl)amino)-4-(1H-pyrrolo[2,3-b]pyridin-1-yl)benzoate: 3da was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (25.7 mg, 70%). **R*f*** = 0.43; **m.p.** = 106–107 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.75 (d, *J* = 2.0 Hz, 1H), 8.42 (dd, *J* = 4.7, 1.7 Hz, 1H), 8.08 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.01 (s, 1H), 7.93 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.42 (d, *J* = 3.6 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.25 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.79 (d, *J* = 3.6 Hz, 1H), 4.01 (s, 3H), 1.49 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 166.4, 153.1, 148.0, 143.7, 133.9, 133.6, 130.0, 129.9, 129.4, 127.3, 125.5, 125.4, 121.6, 117.1, 103.5, 80.7, 52.3, 28.2 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3072, 2962, 1722, 1603, 1485, 1372, 1229, 1054, 713; **HRMS** (ESI) m/z: calculated for $C_{20}H_{21}N_3O_4$ [M+H]$^+$ 368.1605, found 368.1596.



3ea

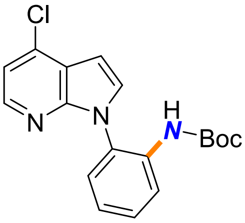
tert*-Butyl (5-fluoro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ea** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (26.8 mg, 82%). **R*f = 0.53; **m.p.** = 124–125 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.39 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.00

(dd, J = 11.0, 2.8 Hz, 1H), 7.44 (s, 1H), 7.33 (d, J = 3.6 Hz, 1H), 7.23 (ddd, J = 8.1, 5.2, 3.5 Hz, 2H), 6.90 (ddd, J = 8.7, 7.5, 2.9 Hz, 1H), 6.75 (d, J = 3.6 Hz, 1H), 1.47 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 162.3 (d, J = 244.6 Hz), 152.6, 148.2, 143.8, 136.2, 136.1, 129.6 (d, J = 24.4 Hz), 128.9 (d, J = 10.0 Hz), 124.4, 121.2, 116.9, 110.4 (d, J = 23.0 Hz), 109.5 (d, J = 28.0 Hz), 102.7, 81.0, 28.2 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3069, 2962, 1732, 1603, 1490, 1234, 1048, 711; **HRMS** (ESI) m/z: calculated for $C_{18}H_{19}FN_3O_2$ [M+H]$^+$ 328.1456, found 328.1452.



3fa

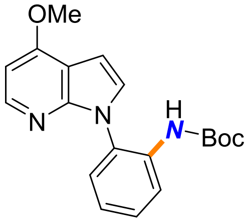
***tert*-Butyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)naphthalen-1-yl)carbamate: 3fa** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (25.5 mg, 71%). **R$_f$** = 0.47; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 8.36 (dd, J = 4.8, 1.6 Hz, 1H), 8.05 (dd, J = 7.9, 1.6 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.78 – 7.71 (m, 2H), 7.55 (s, 1H), 7.49 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.20 (dd, J = 7.9, 4.7 Hz, 1H), 6.75 (d, J = 3.5 Hz, 1H), 1.44 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 153.3, 143.9, 136.1, 133.4, 132.0, 130.2, 129.9, 129.8, 127.6, 127.3, 126.8, 126.7, 125.5, 121.4, 119.9, 116.9, 102.7, 80.6, 28.3 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3068, 2964, 1723, 1613, 1507, 1485, 1229, 1054, 711; **HRMS** (ESI) m/z: calculated for $C_{22}H_{22}N_3O_2$ [M+H]$^+$ 360.1707, found 360.1704.



3ga

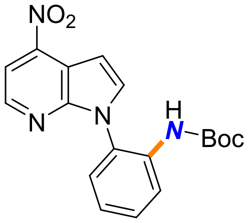
***tert*-Butyl (2-(4-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ga** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (31.2 mg, 91%). **R$_f$** = 0.62; **m.p.** = 50–51 ^{o}C; **^{1}H NMR** (400

MHz, $CDCl_3$): δ = 8.23 (d, *J* = 5.2 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.43 (ddd, *J* = 8.4, 7.1, 1.8 Hz, 1H), 7.37 (d, *J* = 3.6 Hz, 1H), 7.35 (s, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 6.80 (d, *J* = 3.6 Hz, 1H), 1.41 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 153.1, 148.5, 144.0, 136.9, 134.1, 130.2, 129.0, 128.9, 127.6, 124.3, 123.8, 120.6, 117.0, 101.0, 80.6, 28.2 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3086, 2988, 1723, 1603, 1507, 1485, 1199, 1054, 833, 711; **HRMS** (ESI) m/z: calculated for $C_{18}H_{19}ClN_3O_2$ [M+H]$^+$ 344.1160, found 344.1164.



3ha

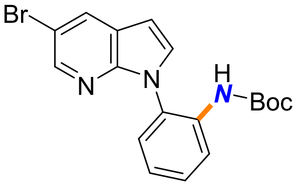
tert*-Butyl (2-(4-methoxy-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ha** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (31.2 mg, 92%). **R*f = 0.62; **m.p.** = 123–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 5.6 Hz, 1H), 8.04 (s, 1H), 7.74 (s, 1H), 7.41 (ddd, *J* = 8.5, 7.3, 1.7 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.22 – 7.14 (m, 2H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.65 (d, *J* = 5.6 Hz, 1H), 4.05 (s, 3H), 1.41 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 160.4, 153.3, 149.6, 145.7, 133.9, 129.5, 128.4, 127.5, 127.4, 124.2, 123.7, 111.4, 99.8, 98.9, 80.3, 55.7, 28.2 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3082, 1722, 1575, 1485, 1229, 1073, 717; **HRMS** (ESI) m/z: calculated for $C_{19}H_{22}N_3O_3$ [M+H]$^+$ 340.1656, found 340.1654.



3ia

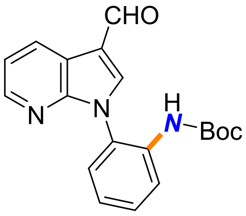
tert*-Butyl (2-(4-nitro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ia** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (30.1 mg, 85%). **R*f = 0.56; **m.p.** = 128–129 °C; **^{1}H NMR** (400

MHz, $CDCl_3$): δ = 8.54 (d, J = 5.3 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 5.3 Hz, 1H), 7.65 (d, J = 3.5 Hz, 1H), 7.49 (ddd, J = 8.5, 6.8, 2.0 Hz, 1H), 7.40 (d, J = 3.5 Hz, 1H), 7.29 – 7.25 (m, 2H), 6.86 (s, 1H), 1.40 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 152.9, 151.3, 146.4, 143.8, 134.6, 134.3, 129.6, 128.2, 127.8, 124.5, 123.8, 114.1, 110.8, 102.6, 80.9, 28.2 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3045, 2935, 1730, 1593, 1494, 1375, 1256, 1083, 717; **HRMS** (ESI) m/z: calculated for $C_{18}H_{18}N_4O_4$ $[M+H]^+$ 355.1401, found 355.1392.



3ja

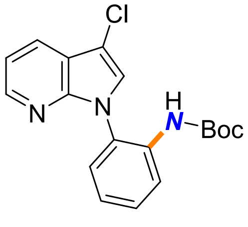
***tert-butyl (2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate*: 3ja** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (35.6 mg, 92%). **R_f** = 0.54; **m.p.** = 121–122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 2.2 Hz, 1H), 8.17 (d, J = 2.1 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.47 (ddd, J = 8.6, 7.0, 2.0 Hz, 1H), 7.39 (d, J = 3.6 Hz, 1H), 7.28 – 7.21 (m, 3H), 6.69 (d, J = 3.6 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, CDCl3): δ = 153.1, 146.5, 144.2, 134.2, 131.7, 131.1, 128.9, 128.8, 127.6, 124.3, 123.7, 122.8, 112.7, 102.0, 80.7, 28.2.; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3056, 2926, 1730, 1485, 1247, 1037, 818, 690; **HRMS** (ESI) m/z: calculated for $C_{18}H_{19}BrN_3O_2$ $[M+H]^+$ 388.0655, found 388.0659.



3ka

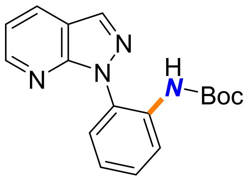
***tert*-Butyl (2-(3-formyl-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3ka** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure productas a white solid (25.3 mg, 75%). **R_f** = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 10.09 (s, 1H), 8.69 (dd, J = 7.9, 1.7 Hz, 1H), 8.45 (dd, J = 4.7, 1.7 Hz, 1H), 8.09 – 7.95 (m, 2H), 7.89 (d, J = 9.1 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.43 – 7.34 (m, 2H), 7.33 – 7.28

(m, 1H), 1.38 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 186.1, 154.1, 148.7, 144.9, 141.5, 134.4, 130.9, 130.6, 129.4, 128.1, 126.1, 125.8, 119.0, 117.8, 117.6, 79.9, 27.0 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3053, 2936, 2723, 1730, 1717, 1485, 1247, 1037, 715; **HRMS** (ESI) m/z: calculated for $C_{19}H_{20}N_3O_3$ [M+H]$^+$ 338.1499, found 338.1493.



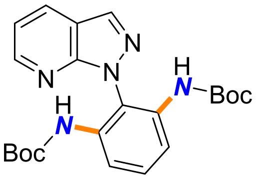
3la

tert*-Butyl (2-(3-chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3la** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (27.1 mg, 79%). **R*f = 0.46; **m.p.** = 126–127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.35 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 (s, 1H), 7.41 (td, *J* = 8.3, 7.8, 1.7 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.20 – 7.12 (m, 2H), 6.69 (d, *J* = 3.6 Hz, 1H), 1.40 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 153.2, 148.1, 143.7, 134.1, 129.7, 129.7, 129.5, 128.4, 127.5, 124.2, 123.7, 121.3, 116.7, 102.5, 80.4, 28.2 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3045, 2926, 1717, 1593, 1485, 1289, 1087, 834, 698; **HRMS** (ESI) m/z: calculated for $C_{18}H_{19}ClN_3O_2$ [M+H]$^+$ 344.1160, found 344.1163.



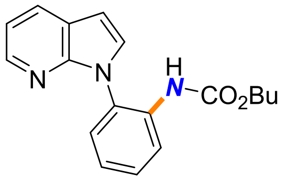
3ma

tert*-Butyl (2-(1H-pyrazolo[3,4-b]pyridin-1-yl)phenyl)carbamate: 3ma** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (28.2 mg, 91%). **R*f = 0.56; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.66 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.37 (s, 1H), 8.34 (s, 1H), 8.22 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 (ddd, *J* = 8.6, 7.4, 1.6 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.24 (td, *J* = 7.7, 1.4 Hz, 1H), 1.47 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 152.8, 150.7, 149.8, 134.7, 133.1, 130.7, 128.5, 127.3, 126.2, 123.2, 122.1, 117.9, 116.3, 80.4, 28.3 ppm. **IR** (KBr): ṽ/cm^{-1} = 3042, 2967, 1737, 1608, 1487, 1297, 1088, 734; **HRMS** (ESI) m/z: calculated for $C_{17}H_{19}N_4O_2$ $[M+H]^+$ 311.1503, found 311.1509.



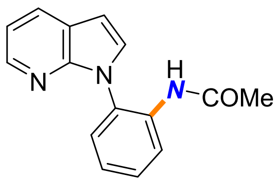
3ma'

Di-*tert*-butyl (2-(1H-pyrazolo[3,4-b]pyridin-1-yl)-1,3-phenylene)dicarbamate: 3ma' was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (31.9 mg, 75%). **R*f***= 0.46; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.66 (dd, *J* = 4.6, 1.6 Hz, 1H), 8.45 (s, 1H), 8.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.92 – 7.77 (m, 2H), 7.46 (t, *J* = 8.3 Hz, 1H), 7.34 (dd, *J* = 8.1, 4.5 Hz, 1H), 6.86 (s, 2H), 1.39 (s, 18H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 152.5, 151.0, 150.4, 136.4, 135.3, 131.2, 129.8, 118.9, 118.2, 117.4, 116.0, 80.6, 28.2. **IR** (KBr): ṽ/cm^{-1} = 3073, 2969, 1737, 1604, 1500, 1297, 1120, 730; **HRMS** (ESI) m/z: calculated for $C_{22}H_{28}N_5O_4$ $[M+H]^+$ 426.2136, found 426.2139.



3af

Butyl (2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)carbamate: 3af was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (27.2 mg, 88%). **R*f***= 0.39; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.36 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.86 (s, 1H), 7.43 (td, *J* = 8.2, 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 3.6 Hz, 1H), 7.26 (s, 1H), 7.22 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.17 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 1.58 – 1.49 (m, 2H), 1.33 – 1.28 (m, 2H), 0.88 (d, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 154.2, 148.0, 143.7, 133.7, 129.9, 129.6, 128.5, 127.4, 124.6, 124.0, 121.4, 116.8, 102.7, 65.1, 30.9, 29.7, 19.0, 13.6; **IR** (KBr): ṽ/cm^{-1} = 3033, 2989, 1730, 1604, 1500, 1465, 1297, 1375, 1089, 731; **HRMS** (ESI) m/z: calculated for $C_{18}H_{20}N_3O_2$ $[M+H]^+$ 310.1550, found 310.1555.

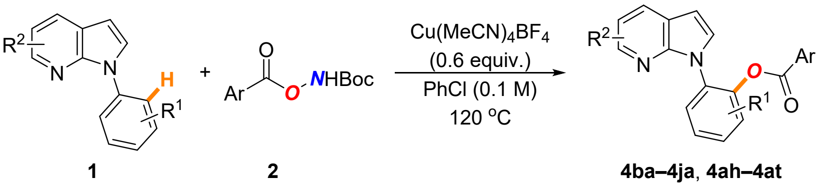


3ag

N-**(2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl)acetamide: 3ag** was prepared according to **GP A,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (20.8 mg, 83%). **R*f*** = 0.42; **m.p.** = 126–127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 9.11 (s, 1H), 8.27 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.04 – 7.81 (m, 2H), 7.36 (ddd, *J* = 8.4, 6.5, 2.3 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.11 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.63 (d, *J* = 3.6 Hz, 1H), 1.85 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 168.6, 147.8, 143.1, 132.9, 130.9, 130.2, 130.0, 128.1, 127.1, 126.1, 125.7, 121.7, 116.8, 102.9, 24.2; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3083, 2917, 1730, 1593, 1475, 1375, 1256, 1083, 726; **HRMS** (ESI) m/z: calculated for $C_{15}H_{13}N_3O$ $[M+H]^+$ 252.1132, found 252.1124.

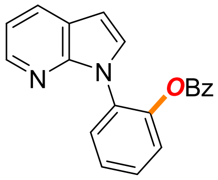
4 Experimental Details for Copper Enabled Aroyloxylation Reactions

4.1 General Procedure for the Aroyloxylation Reactions (GP B)



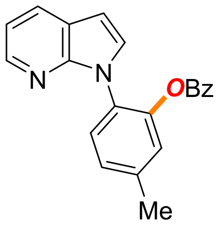
To a solution of *N*-aryl-7-azaindole **1** (0.1 mmol) in chlorobenzene (1.0 mL), $Cu(Me_3CN)_4BF_4$ (19 mg, 60 mol%) was added aroyloxylation **2** and stirred vigorously at 120 °C for 12 h. After completion of the reaction, the mixture was filtered through a short celite pad and concentrated under vacuum. The residual was purified through column chromatography using hexane/ethylacetate as eluent to give oxygenation products.

4.2 Characterization Data of the Aroyloxylation Products



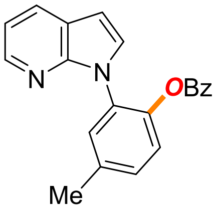
4aa

(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4aa was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (26.7 mg, 85%). **R*f*** = 0.43; **m.p.** = 90–91 °C; **^{1}H NMR** (600 MHz, MeOD): *δ* = 8.13 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.64 (dq, *J* = 8.0, 1.6 Hz, 3H), 7.61 – 7.57 (m, 1H), 7.50 (dddd, *J* = 7.5, 6.1, 4.9, 1.4 Hz, 3H), 7.42 (d, *J* = 3.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.08 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H) ppm; **^{13}C NMR** (151 MHz, MeOD): *δ* = 164.2, 147.4, 146.7, 142.5, 133.4, 130.7, 129.5, 129.5, 129.3, 129.0, 128.6, 128.5, 128.1, 126.7, 123.7, 121.3, 116.3, 101.4 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 2548, 2177, 1738, 1619, 1510, 1256, 1219, 1046, 749; **HRMS** (ESI) m/z: calculated for $C_{20}H_{14}N_2O_2$ $[M+H]^+$ 315.1128, found 315.1119.



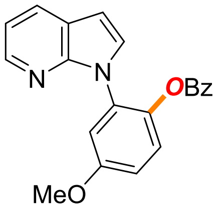
4ba

5-Methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ba was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (21.3 mg, 65%). **R$_f$** = 0.34; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.36 (t, J = 3.6 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.7 Hz, 2H), 7.61 – 7.50 (m, 2H), 7.36 (d, J = 7.0 Hz, 4H), 7.32 (s, 1H), 7.13 – 7.04 (m, 1H), 6.55 (d, J = 3.4 Hz, 1H), 2.53 (s, 3H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 164.7, 148.2, 145.9, 143.7, 139.4, 133.4, 129.9, 129.2, 128.9, 128.9, 128.4, 128.3, 128.0, 127.5, 124.4, 120.6, 116.4, 101.3, 21.3 ppm； **IR** (KBr): ṽ/cm^{-1} = 3069, 1700, 1530, 1329, 1212, 1066, 755; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_2$ [M+H]$^+$ 329.1285, found 329.1283.



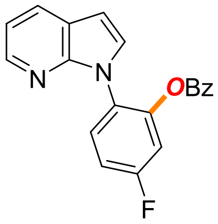
4ca

4-Methyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ca was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (18.0 mg, 55%). **R$_f$** = 0.35; **m.p.** = 94–95 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.36 (d, J = 4.7 Hz, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.7 Hz, 2H), 7.58 – 7.47 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.38 – 7.34 (m, 4H), 7.10 (t, J = 6.1 Hz, 1H), 6.56 (d, J = 3.7 Hz, 1H), 2.52 (s, 3H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 164.8, 148.1, 143.9, 143.7, 136.7, 133.4, 130.3, 129.9, 129.6, 129.2, 129.2, 129.0, 128.9, 128.3, 123.6, 120.7, 116.4, 101.4, 21.0 ppm; **IR** (KBr): ṽ/cm^{-1} = 3075, 1715, 1625, 1500, 1250, 1096, 725; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_2$ [M+H]$^+$ 329.1285, found 329.1281.



4da

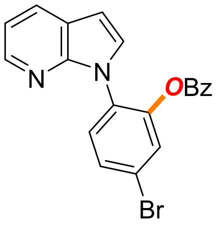
4-Methoxy-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4da was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (18.2 mg, 53%). **R_f** = 0.43; **m.p.** = 91–92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.36 (dd, J = 4.6, 1.8 Hz, 1H), 7.91 (dt, J = 7.8, 1.7 Hz, 1H), 7.79 (dt, J = 8.5, 1.6 Hz, 2H), 7.52 (td, J = 7.4, 1.6 Hz, 1H), 7.42 (dd, J = 9.1, 1.6 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.23 (dd, J = 3.1, 1.6 Hz, 1H), 7.09 (dq, J = 8.8, 2.9 Hz, 2H), 6.56 (dd, J = 3.6, 1.6 Hz, 1H), 3.91 (d, J = 1.7 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 165.1, 157.8, 148.1, 143.9, 139.7, 133.5, 131.3, 130.0, 129.1, 129.1, 128.4, 124.6, 120.8, 116.6, 114.4, 113.9, 101.7, 55.9 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 2540, 2177, 1988, 1738, 1617, 1514, 1254, 1212, 1048, 747; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_3$ $[M+H]^+$ 345.1234, found 345.1229.



4ea

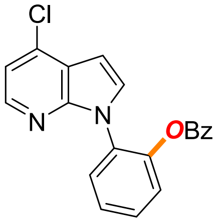
5-Fluoro-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ea was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (25.9 mg, 78%). **R_f** = 0.46; **m.p.** = 105–106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.33 (dd, J = 4.7, 1.7 Hz, 1H), 7.91 (dd, J = 7.9, 1.6 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.65 (dd, J = 8.8, 5.7 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.36 – 7.30 (m, 4H), 7.21 (ddd, J = 8.9, 7.7, 2.8 Hz, 1H), 7.09 (dd, J = 7.8, 4.7 Hz, 1H), 6.56 (d, J = 3.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.1, 161.9 (d, J = 247.8 Hz), 148.1, 147.1, 147.0, 143.8, 133.7, 130.0, 129.7, 129.6, 129.0 (d, J = 2.9 Hz), 128.4, 127.0, 120.6, 116.6, 113.7 (d, J = 22.3 Hz), 111.9 (d, J = 25.5 Hz), 101.7 ppm; **^{19}F NMR** (37 MHz, $CDCl_3$): δ = -62.32 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3057, 2936, 1747, 1514, 1436, 1255, 1117, 1040, 764, 695;

HRMS (ESI) m/z: calculated for $C_{20}H_{13}FN_2O_2$ $[M+H]^+$ 333.1034, found 333.1028.



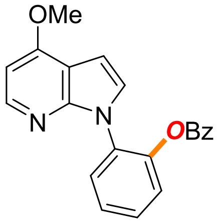
4fa

5-Bromo-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4fa was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a white solid (29.0 mg, 74%). **R$_f$**= 0.52; **m.p.** = 84–85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.33 (dd, *J* = 4.7, 1.5 Hz, 1H), 7.91 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.80 – 7.75 (m, 2H), 7.72 (d, *J* = 1.9 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.38 – 7.32 (m, 3H), 7.10 (ddd, *J* = 7.8, 4.7, 1.0 Hz, 1H), 6.57 (dd, *J* = 3.6, 1.0 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.1, 147.9, 146.5, 143.8, 133.7, 130.0, 129.9, 129.8, 129.7, 129.1, 128.7, 128.4, 128.3, 127.4, 121.4, 120.7, 116.8, 102.0 ppm; **IR** (KBr): ṽ/cm^{-1} = 2935, 1740, 1503, 1238, 1047, 836, 700; **HRMS** (ESI) m/z: calculated for $C_{20}H_{14}BrN_2O_2$ $[M+H]^+$ 393.0233, found 393.0238.



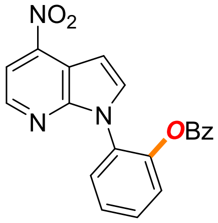
4ga

2-(4-Chloro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ga was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (22.6 mg, 65%). **R$_f$**= 0.42; **m.p.** = 123–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 5.1 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.54 (dq, *J* = 15.0, 7.6 Hz, 4H), 7.44 – 7.34 (m, 3H), 7.12 (d, *J* = 5.1 Hz, 1H), 6.68 (d, *J* = 3.7 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.5, 148.6, 146.1, 144.1, 136.1, 133.6, 130.3, 130.0, 129.7, 129.2, 128.7, 128.6, 128.4, 126.8, 124.1, 120.0, 116.7, 100.1 ppm; **IR** (KBr): ṽ/cm^{-1} = 2955, 1730, 1500, 1238, 1045, 852, 710; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}ClN_2O_2$ $[M+H]^+$ 349.0739, found 349.0736.



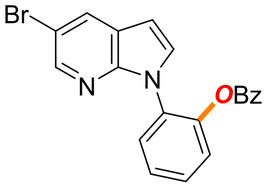
4ha

2-(4-Methoxy-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ha was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (19.6 mg, 57%). **R$_f$** = 0.38; **m.p.** = 88–89 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.26 (t, J = 4.1 Hz, 1H), 7.86 (d, J = 7.3 Hz, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.38 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 3.5 Hz, 1H), 6.67 (d, J = 3.4 Hz, 1H), 6.58 (t, J = 4.3 Hz, 1H), 4.02 (d, J = 2.9 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 164.5, 159.8, 149.7, 146.1, 145.7, 133.4, 130.8, 130.0, 128.9, 128.8, 128.7, 128.3, 126.8, 126.7, 124.0, 110.9, 98.9, 98.5, 55.5 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 2548, 2177, 2039, 1970, 1212, 1075, 755; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_3$ [M+H]$^+$ 345.1234, found 345.1226.



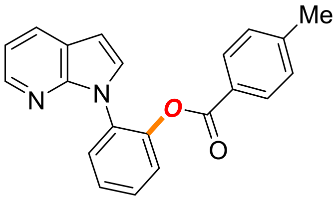
4ia

2-(4-Nitro-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ia was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (17.3 mg, 48%). **R$_f$**= 0.35; **m.p.** = 122–123 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.51 (d, J = 5.3 Hz, 1H), 7.91 (d, J = 5.3 Hz, 1H), 7.80 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 3.7 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.65 – 7.61 (m, 1H), 7.59 – 7.52 (m, 3H), 7.37 (t, J = 7.7 Hz, 2H), 7.28 (d, J = 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 164.3, 151.3, 146.2, 145.9, 143.6, 134.1, 133.8, 129.9, 129.8, 129.7, 128.7, 128.5, 128.4, 126.9, 124.2, 113.5, 110.5, 101.7 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3073, 2916, 1721, 1593, 1494, 1255, 1073, 726; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}N_3O_4$ [M+H]$^+$ 360.0979, found 360.0972.



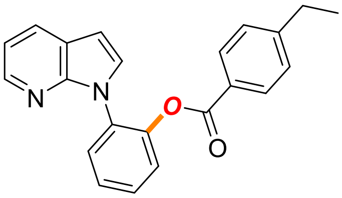
4ja

2-(5-Bromo-1H-pyrrolo[2,3-b]pyridin-1-yl)phenyl benzoate: 4ja was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (28.3 mg, 72%). **R*f***= 0.33; **m.p.** = 130–131 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.35 (s, 1H), 8.02 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 14.0 Hz, 3H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 3H), 6.50 (d, *J* = 3.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 164.5, 146.4, 146.2, 144.2, 133.7, 131.0, 130.6, 130.3, 130.0, 129.2, 128.7, 128.4, 126.8, 125.5, 124.1, 122.3, 112.5, 101.1 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3073, 1722, 1585, 1485, 1238, 1064, 709; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}BrN_2O_2$ $[M+H]^+$ 393.0233, found 393.0226.



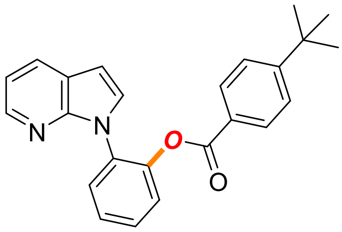
4ah

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-methylbenzoate: 4ah was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (26.6 mg, 81%). **R*f***= 0.63; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.36 (d, *J* = 4.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 19.2 Hz, 4H), 7.34 (dd, *J* = 14.7, 5.5 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.55 (d, *J* = 3.6 Hz, 1H), 2.30 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 164.7, 148.2, 145.9, 143.7, 139.4, 133.4, 129.9, 129.2, 128.9, 128.8, 128.4, 128.3, 128.0, 127.5, 124.4, 120.6, 116.4, 101.3, 21.3 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3073, 1710, 1619, 1485, 1234, 1084, 723; **HRMS** (ESI) m/z: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1286.



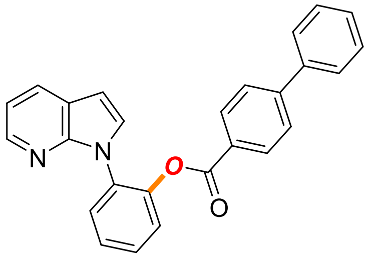
4ai

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-ethylbenzoate: 4ai was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (28.4 mg, 83%). **R*f*** = 0.63; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.37 (d, *J* = 4.7 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.9 Hz, 3H), 7.53 (dq, *J* = 14.3, 7.6 Hz, 3H), 7.38 (d, *J* = 3.7 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.11 (dd, *J* = 8.3, 4.8 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 2.69 (q, *J* = 7.7 Hz, 2H), 1.26 (t, *J* = 7.7 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 164.6, 150.5, 148.1, 146.2, 143.7, 130.7, 130.2, 129.1, 128.9, 128.8, 128.7, 127.9, 126.6, 126.3, 124.1, 120.7, 116.5, 101.5, 29.0, 15.1 ppm; **HRMS** (ESI) m/z: calculated for $C_{22}H_{18}N_2O_2$ $[M+H]^+$ 343.1441, found 343.1434.



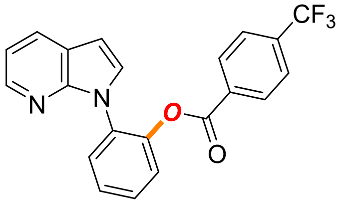
4aj

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-(*tert*-butyl)benzoate: 4aj was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (32.5 mg, 88%). **R*f*** = 0.64; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.38 (d, *J* = 4.7 Hz, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.53 (h, *J* = 8.9, 8.3 Hz, 3H), 7.38 (d, *J* = 8.8 Hz, 3H), 7.12 (dd, *J* = 8.2, 4.4 Hz, 1H), 6.58 (q, *J* = 2.7 Hz, 1H), 1.35 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 164.6, 157.3, 148.1, 146.2, 143.7, 130.7, 130.9, 129.9, 129.2, 128.9, 128.8, 126.6, 126.1, 125.4, 124.1, 120.7, 116.5, 101.5, 35.1, 31.1 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3073, 1722, 1580, 1490, 1245, 1068, 715; **HRMS** (ESI) m/z: calculated for $C_{24}H_{22}N_2O_2$ $[M+H]^+$ 371.1754, found 371.1746.



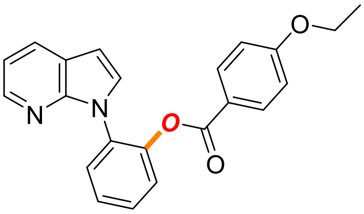
4ak

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl[1,1'-biphenyl]-4-carboxylate: **4ak** was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (27.3 mg, 70%). **R*f*** = 0.38; **m.p.** = 99–100 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.32 (d, *J* = 4.6 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.04 (dd, *J* = 8.1, 4.5 Hz, 1H), 6.52 (d, *J* = 3.5 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 164.4, 148.1, 146.2, 146.1, 143.8, 139.8, 130.7, 130.5, 129.1, 129.0, 128.9, 128.8, 128.6, 128.3, 127.6, 127.3, 127.0, 126.7, 124.1, 120.7, 116.6, 101.6 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 2380, 2075, 2010, 1850, 1200, 735; **HRMS** (ESI) m/z: calculated for $C_{26}H_{18}N_2O_2$ [M+H]$^+$ 391.1441, found 391.1437.



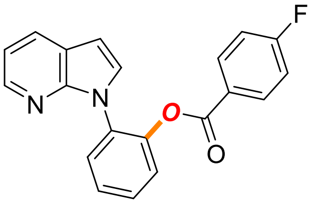
4al

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-(trifluoromethyl)benzoate: **4al** was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a white solid (25.9 mg, 68%). **R*f*** = 0.52; **m.p.** = 103–104 °C; **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 8.32 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.49 (m, 3H), 7.37 (d, *J* = 3.6 Hz, 1H), 7.09 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.59 (d, *J* = 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, CDCl$_3$): δ = 163.3, 148.0, 145.9, 143.8, 134.7 (q, *J* = 32.5 Hz), 132.1, 130.6, 130.3, 129.1, 128.9, 128.9, 128.7, 127.1, 125.3 (d, *J* = 3.6 Hz), 123.8, 123.4 (d, *J* = 271.1 Hz), 120.7, 116.6, 101.8 ppm; **^{19}F NMR** (376 MHz, CDCl$_3$): δ = -63.18 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3074, 1764, 1531, 1333, 1272, 1212, 1135, 1066, 859, 755; **HRMS** (ESI) m/z: calculated for $C_{21}H_{13}F_3N_2O_2$ $[M+H]^+$ 383.1002, found 383.0995.



4am

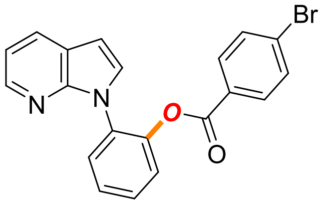
2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-ethoxybenzoate: 4am was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (29.4 mg, 82%). $\mathbf{R}_f$= 0.58; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.36 (d, *J* = 4.2 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.51 (h, *J* = 7.9 Hz, 3H), 7.37 (d, *J* = 3.8 Hz, 1H), 7.09 (dt, *J* = 7.5, 3.1 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 3.7 Hz, 1H), 4.07 (q, *J* = 7.4 Hz, 2H), 1.44 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 164.3, 163.2, 148.1, 146.3, 143.7, 132.1, 130.7, 129.2, 128.9, 128.8, 128.7, 126.5, 124.1, 120.9, 120.7, 116.5, 114.0, 101.4, 63.7, 14.6 ppm; **HRMS** (ESI) m/z: calculated for $C_{22}H_{18}N_2O_3$ $[M+H]^+$ 359.1390, found 359.1383.



4an

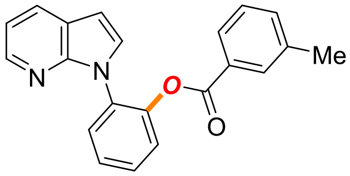
2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-fluorobenzoate: 4an was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (20.9 mg, 63%). $\mathbf{R}_f$= 0.45; **m.p.** = 128–129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.34 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.85 – 7.74 (m, 2H), 7.69 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.60 – 7.47 (m, 3H), 7.36 (d, *J* = 3.6 Hz, 1H), 7.09 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 3.6 Hz, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$): *δ* = 165.9 (d, *J* = 261.3 Hz), 163.5, 148.0, 146.1, 143.7, 132.5 (d, *J* = 9.7 Hz), 130.7, 129.0 (d, *J* = 25.0 Hz), 129.0, 128.7, 126.8, 125.1 (d, *J* = 2.3 Hz), 124.0, 120.7, 116.5, 115.6, 115.5, 101.6 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) : *δ* = -100.32

ppm; **IR** (KBr): ṽ/cm^{-1} = 3048, 1754, 1608, 1513, 1427, 1247, 1220, 1135, 1057, 747; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}FN_2O_2$ [M+H]$^+$ 333.1034, found 333.1028.



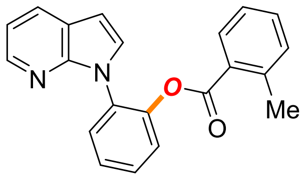
4ao

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 4-bromobenzoate: 4ao was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (26.7 mg, 68%). **R$_f$**= 0.48; **m.p.** = 118–119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.28 (d, *J* = 4.6 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.05 (dd, *J* = 8.2, 4.7 Hz, 1H), 6.53 (d, *J* = 3.5 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 163.8, 148.0, 146.0, 143.8, 131.7, 131.4, 130.6, 129.7, 129.2, 129.0, 128.9, 128.7, 127.8, 126.9, 123.9, 120.7, 116.6, 101.7 ppm; **IR** (KBr): ṽ/cm^{-1} = 3069, 1710, 1080, 1475, 1200, 1075, 831, 715; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}BrN_2O_2$ [M+H]$^+$ 393.0233, found 393.0239.



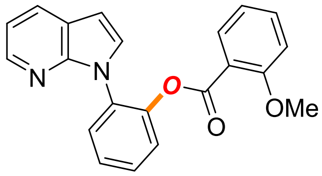
4ap

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 3-methylbenzoate: 4ap was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 5% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (22.1 mg, 67%). **R$_f$**= 0.62; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.40 (d, *J* = 4.6 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 20.2 Hz, 4H), 7.42 – 7.34 (m, 2H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.14 (dd, *J* = 8.2, 4.5 Hz, 1H), 6.59 (d, *J* = 3.8 Hz, 1H), 2.34 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$): *δ* = 164.7, 148.1, 146.3, 143.7, 138.1, 134.2, 130.7, 130.5, 129.2, 128.9, 128.9, 128.8, 128.7, 128.2, 127.1, 126.7,124.0, 120.7, 116.5, 101.6, 21.1 ppm. **IR** (KBr): ṽ/cm^{-1} = 3075, 1705, 1625, 1500, 1247, 1112, 719; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1281.



4aq

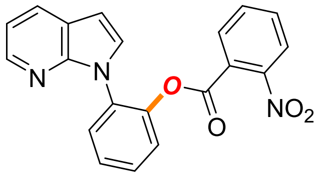
2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 2-methylbenzoate: 4aq was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (20.4 mg, 62%). **R_f** = 0.54; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.37 (dd, J = 4.7, 1.6 Hz, 1H), 7.94 (dd, J = 7.8, 1.6 Hz, 1H), 7.70 (dd, J = 8.1, 1.7 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.40 – 7.34 (m, 2H), 7.20 (d, J = 7.6 Hz, 1H), 7.10 (td, J = 7.9, 5.7 Hz, 2H), 6.58 (d, J = 3.6 Hz, 1H), 2.45 (s, 3H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$): δ = 165.0, 148.2, 146.4, 143.7, 141.2, 132.6, 131.6, 130.8, 130.9, 129.2, 129.0, 128.9, 128.8, 127.8, 126.7, 125.6, 124.1, 120.7, 116.5, 101.5, 21.5 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3082, 1715, 1620, 1505, 1238, 1096, 720; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1279.



4ar

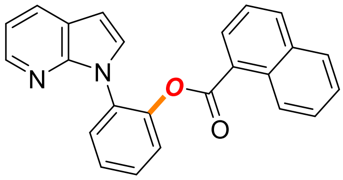
2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 2-methoxybenzoate: 4ar was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a white solid (25.8 mg, 75%). **R_f** = 0.41; **m.p.** = 101–102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.32 (dd, J = 4.7, 1.6 Hz, 1H), 7.90 (dd, J = 7.8, 1.6 Hz, 1H), 7.64 (dd, J = 7.7, 1.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H), 7.40 – 7.34 (m, 2H), 7.29 (dd, J = 7.8, 1.8 Hz, 1H), 7.07 (dd, J = 7.8, 4.7 Hz, 1H), 6.90 – 6.82 (m, 1H), 6.75 (td, J = 7.5, 1.0 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 3.73 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 163.6, 153.6, 159.8, 148.2, 146.3, 143.7, 134.3, 132.0, 130.8, 129.4, 128.9, 128.8, 126.6, 124.3, 120.7, 119.9, 118.2, 116.5, 111.9, 101.3, 55.8 ppm; **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 2514, 2177, 2005, 1212, 1040, 738, 670; **HRMS** (ESI) m/z: calculated for $C_{21}H_{16}N_2O_3$

$[M+H]^+$ 345.1234, found 345.1229.



4as

(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 2-nitrobenzoate: 4as was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow oil (20.5 mg, 57%). **R*f*** = 0.63; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.34 (d, *J* = 4.7 Hz, 1H), 7.98 (t, *J* = 9.6 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.64 – 7.55 (m, 3H), 7.50 (dt, *J* = 14.6, 7.5 Hz, 2H), 7.40 (d, *J* = 3.8 Hz, 1H), 7.13 (d, *J* = 6.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 3.8 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 163.4, 148.0, 147.3, 145.6, 143.9, 133.1, 131.7, 130.7, 129.3, 129.2, 129.0, 128.8, 128.9, 127.4, 127.1, 124.1, 123.5, 120.7, 116.6, 101.7 ppm; **IR** (KBr): ṽ/cm^{-1} = 3085, 2900, 1735, 1615, 1567, 1500, 1345, 1258, 1085, 735; **HRMS** (ESI) m/z: calculated for $C_{20}H_{13}N_3O_4$ $[M+H]^+$ 360.0979, found 360.0978.

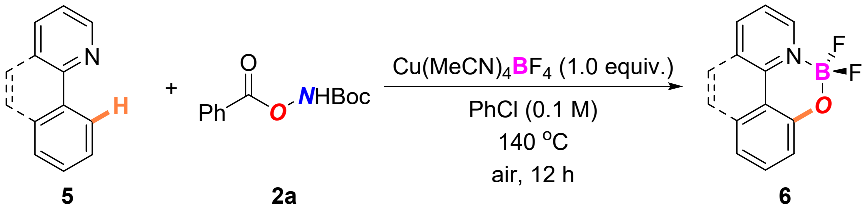


4at

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenyl 1-naphthoate: 4at was prepared according to **GP B,** The crude reaction mixture was purified by column chromatography using 10% ethyl acetate in hexane and afforded the analytically pure product as a yellow solid (26.2 mg, 72%). **R*f*** = 0.49; **m.p.** = 150–151 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.83 – 8.67 (m, 1H), 8.38 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.56 – 7.52 (m, 3H), 7.43 (d, *J* = 3.6 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.11 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.56 (d, *J* = 3.8 Hz, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$): *δ* = 165.0, 148.2, 146.5, 143.8, 134.1, 133.7, 131.4, 131.0, 131.0, 129.2, 129.1, 129.0, 128.9, 128.5, 128.0, 126.9, 126.3, 125.5, 125.1, 124.3, 124.2, 120.7, 116.5, 101.6 ppm; **IR** (KBr): ṽ/cm^{-1} = 2385, 2168, 2014, 1970, 1212, 738; **HRMS** (ESI) m/z: calculated for $C_{24}H_{16}N_2O_2$ $[M+H]^+$ 365.1285, found 365.1278.

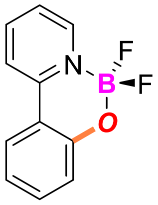
5 Experimental Details for the Difluoroboron Complexes

5.1 General Procedure for the Synthesis of Difluoroboron Complexes (GP C)



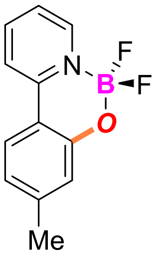
To a solution of heteroarene **5** (1.0 mmol) in chlorobenzene (1.0 mL), $Cu(Me_3CN)_4BF_4$ (31.5 mg, 1.0 equiv.) was added benzoyloxycarbamate **2a** and stirred vigorously at 140 °C for 12 h. After completion of the reaction, the mixture was filtered through a short celite pad and concentrated under vacuum. The residual was purified through column chromatography using hexane/ethylacetate as eluent to give the BF_2 complexes.

5.2 Characterization Data of the Difluoroboron Complexes



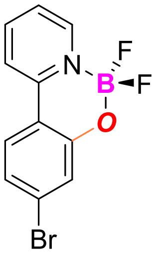
6aa

6,6-Difluoro-6H-6λ⁴,7λ⁴-benzo[e]pyrido[1,2-c][1,3,2]oxazaborinine: 6aa was prepared according to **GP C**, the crude reaction mixture was purified by column chromatography using 30% ethyl acetate in hexane to afford the pure product as a white solid (18.2 mg, 83%). **^{1}H NMR** (400 MHz, DMSO-d$_6$): δ = 8.79 (d, J = 5.8 Hz, 1H), 8.64 (d, J = 8.4 Hz, 1H), 8.52 (t, J = 8.0 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 6.9 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.15 (q, J = 7.8 Hz, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO): δ = 155.3, 149.1, 144.5, 141.5, 134.9, 127.0, 125.1, 122.0, 121.2, 120.1, 116.6 ppm.



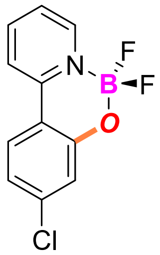
6ba

6,6-Difluoro-3-methyl-6H-6λ⁴,7λ⁴-benzo[e]pyrido[1,2-c][1,3,2]oxazaborinine: 6ba was prepared according to **GP C**, the crude reaction mixture was purified by column chromatography using 30% ethyl acetate in hexane and afforded the analytically pure product as a white solid (17.5 mg, 75%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 5.9 Hz, 1H), 8.18 (td, J = 7.9, 7.3, 1.7 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.57 (t, J = 6.7 Hz, 1H), 7.05 (s, 1H), 6.91 (d, J = 8.2 Hz, 1H), 2.44 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 150.7, 146.3, 142.0, 141.2, 135.7, 125.1, 122.3, 122.1, 121.1, 120.1, 113.9, 21.8 ppm.



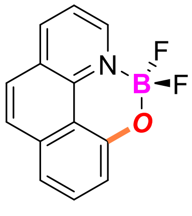
6ca

3-Bromo-6,6-difluoro-6H-6λ⁴,7λ⁴-benzo[e]pyrido[1,2-c][1,3,2]oxazaborinine: 6ca was prepared according to **GP C**, the crude reaction mixture was purified by column chromatography using 30% ethyl acetate in hexane and afforded the analytically pure product as a white solid (20.5 mg, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.70 (d, J = 5.9 Hz, 1H), 8.20 (t, J = 8.0 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.6 Hz, 1H), 7.61 (t, J = 6.8 Hz, 1H), 7.37 (s, 1H), 7.17 (d, J = 8.6 Hz, 1H)ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 156.5, 149.7, 142.5, 141.4, 128.8, 126.3, 124.1, 124.0, 123.2, 120.4, 115.0 ppm.



6da

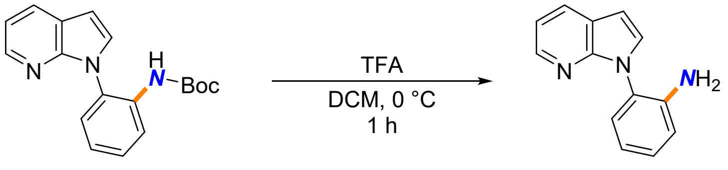
3-Chloro-6,6-difluoro-6H-6λ4,7λ4-benzo[e]pyrido[1,2-c][1,3,2]oxazaborinine: **6da** was prepared according to **GP C**, the crude reaction mixture was purified by column chromatography using 30% ethyl acetate in hexane and afforded the analytically pure product as a white solid (18.2 mg, 72%). **^{1}H NMR** (600 MHz, $CDCl_3$): *δ* = 8.70 (d, *J* = 5.9 Hz, 1H), 8.27 – 8.16 (m, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.62 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.1 Hz, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$): *δ* = 156.6, 149.6, 142.5, 141.4, 140.5, 126.3, 123.2, 121.4, 120.9, 120.4, 114.7 ppm.



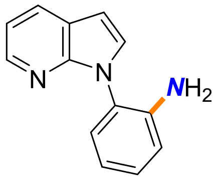
6ea

4,4-Difluoro-4H-5-oxa-3aλ^4-aza-4λ^4-borapyrene: 6ea was prepared according to **GP C**, the crude reaction mixture was purified by column chromatography using 30% ethyl acetate in hexane and afforded the analytically pure product as a white solid (18.5 mg, 76%). **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 9.07 (d, *J* = 5.6 Hz, 1H), 8.67 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.94 (dd, *J* = 8.0, 5.7 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 153.9, 141.0, 140.7, 139.3, 134.5, 133.1, 130.9, 126.8, 123.4, 121.6, 119.0, 116.7, 112.4 ppm.

6 Experimental Details for the Product Derivation

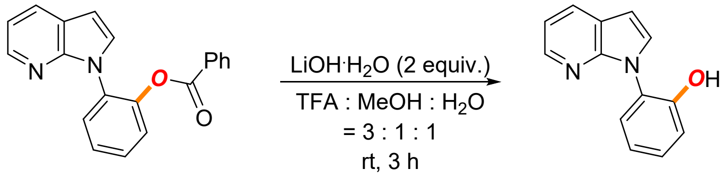


Compound **3aa** (37.1 mg, 0.12 mmol) was dissolved in dichloromethane (2 mL) and cooled to 0 °C. TFA (0.2 mL) was added via syringe and the resulting solution was stirred for 1 h. The reaction mixture was diluted with dichloromethane and washed with $NaHCO_3$, water and brine. The organic layer was evaporated and the crude product purified by column chromatography on silica to give the compound **7** as a brown solid (32.8 mg, 87%).

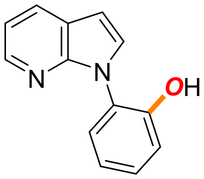


7

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)aniline (7): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (d, *J* = 4.7 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 3.7 Hz, 1H), 7.29 (dd, *J* = 16.7, 7.9 Hz, 2H), 7.18 (t, *J* = 6.5 Hz, 1H), 6.95 (q, *J* = 7.7 Hz, 2H), 6.72 (d, *J* = 3.4 Hz, 1H), 3.98 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 147.7, 143.7, 142.9, 129.6, 129.4, 129.1, 128.4, 124.9, 121.1, 119.1, 117.4, 116.4, 101.7 ppm.

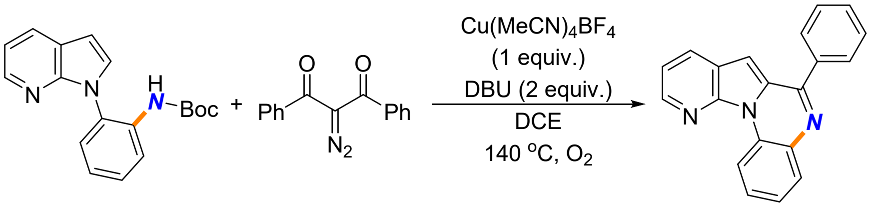


To a solution of **4aa** (31.4 mg, 0.1 mmol) in TFA (1.5 mL), MeOH (0.5 mL), and H_2O (0.5 mL), $LiOH{\cdot}H_2O$ (8.0 mg, 2.0 equiv.) was added. The mixture was stirred at room temperature for 3 h. After completion of the reaction, the reaction mixture was extracted with ethyl acetate (10 mL X 2 times) and brine, evaporated and the residue was purified by column chromatography with (15% EtOAc/hexane) to give the compound **8** as a brown solid.

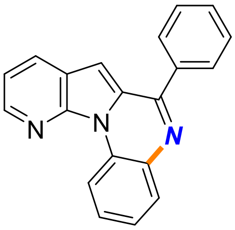


8

2-(1H-Pyrrolo[2,3-b]pyridin-1-yl)phenol (8): (19.7 mg, 94%). **m.p.** = 95–97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 8.16 (d, *J* = 4.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 3.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 6.3 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 149.9, 147.1, 142.0, 130.8, 129.0, 128.4, 128.0, 124.7, 122.4, 121.5, 121.2, 116.4, 103.4 ppm. **IR** (KBr): $\tilde{\nu}$/cm^{-1} = 3183, 2935, 1730, 1503, 1230, 1047, 827, 690; **HRMS** (ESI) m/z: calculated for $C_{13}H_{10}N_2O$ $[M+H]^+$ 211.0866, found 211.0861.



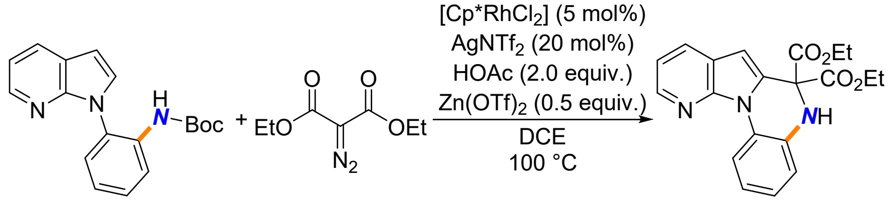
To a solution of amino 7-azaindole **3aa** (0.1 mmol) in DCE (1.0 mL), $Cu(Me_3CN)_4BF_4$ (31.5 mg, 1.0 equiv.), DBU (30.4 mg, 2.0 equiv.) and **9a** (30.1 mg, 1.2 equiv.) were added under O_2, the reaction was stirred at 140 °C for 12 h. After completion of the reaction, the mixture was filtered through a short celite pad and concentrated under vacuum. The residual was purified through column chromatography using hexane/ethyl acetate as eluent to give the compound **10a** as a yellow solid (18.3 mg, 62%).



10a

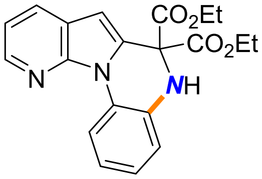
6-Phenylpyrido[3',2':4,5]pyrrolo[1,2-a]quinoxaline (10a): **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 9.90 (d, *J* = 8.3 Hz, 1H), 8.70 (dd, *J* = 4.5, 1.6 Hz, 1H), 8.20 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.07 – 8.02 (m, 2H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.58

(dd, *J* = 5.1, 1.9 Hz, 3H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (dd, *J* = 8.0, 4.5 Hz, 1H), 7.12 (s, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 155.7, 145.5, 144.9, 137.9, 135.7, 130.5, 130.1, 129.7, 129.0, 128.8, 128.6, 128.2, 128.1, 124.8, 121.2, 118.6, 117.6, 99.2 ppm.



3aa **9b** **10b** (43%)

To a solution of amino 7-azaindole **3aa** (0.1 mmol) in DCE (1.0 mL), [Cp*$RhCl_2$] (3.1 mg, 5.0 mol%.), $AgNTf_2$ (7.8 mg, 20 mol%), $Zn(OTf)_2$ (10.7 mg, 0.5 equiv.), HOAc (12.1 mg, 2.0 equiv.), and **9b** (22.3 mg, 1.2 equiv.) were added, the reaction was stirred at 100 °C for 18 h. After completion of the reaction, the mixture was filtered through a short celite pad and concentrated under vacuum. The residual was purified through column chromatography using hexane/ethyl acetate as eluent to give the compound **10b** as a yellow solid (15.7 mg, 43%).

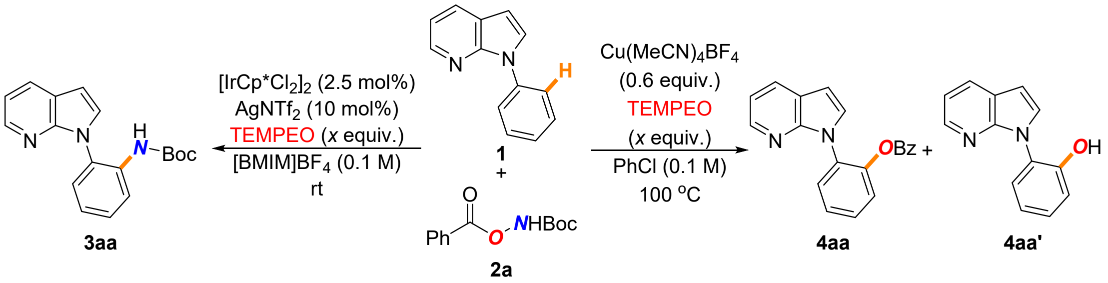


10b

Diethyl pyrido[3',2':4,5]pyrrolo[1,2-a]quinoxaline-6,6(5H)-dicarboxylate (10b): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 9.15 (dd, *J* = 5.9, 3.6 Hz, 1H), 8.56 – 8.40 (m, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.21 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.11 (s, 2H), 7.01 – 6.94 (m, 1H), 6.87 (s, 1H), 5.12 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 4H), 1.32 (t, *J* = 7.2 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$): *δ* = 167.3, 146.9, 143.5, 132.3, 129.9, 129.0, 125.3, 124.8, 121.5, 121.1, 118.9, 117.2, 115.7, 100.2, 66.4, 63.1, 14.1 ppm; **HRMS** (ESI) m/z: calculated for $C_{20}H_{20}N_3O_4$ $[M+H]^+$ 366.1448, found 366.1452.

7 Mechanistic Investigation Experiments

(a) Radical Trapping Experiment

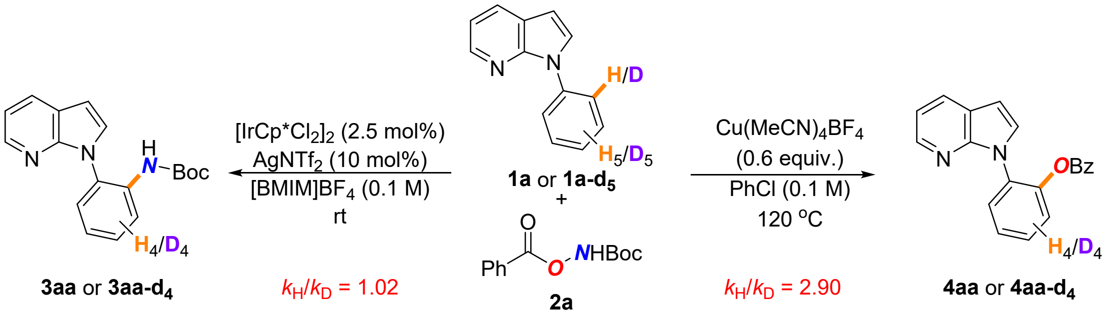


TEMPEO	**3aa** (%)	**4aa** (%)	**4aa'** (%)
none	99	85	0
1 equiv.	87	45	31
2 equiv.	86	41	37

1 equiv. of TEMPO (TEMPO = 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) was added to the reaction mixture of **1a** and **2a**, the reaction was not inhibited in each case. While the generation of hydroxylation product **4aa'** resulted in a dramatically reduced yield of **4aa** with copper. The yields was not further decreased in the presence of 2.0 equiv. of TEMPO.

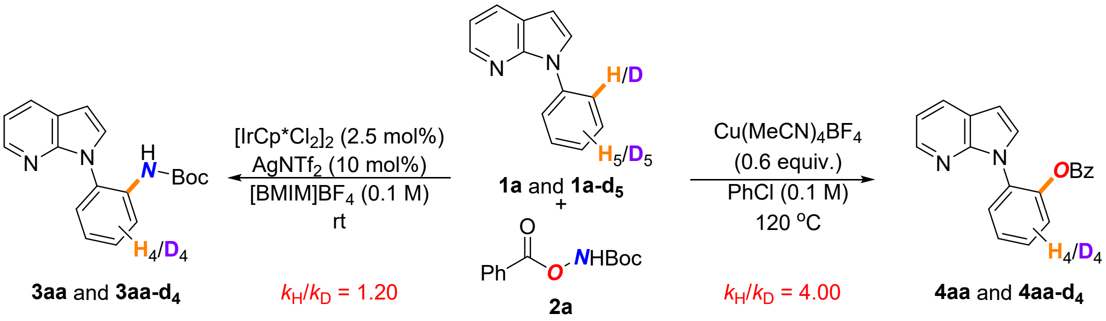
(b) Isotopic Effect Experiments

Procedure for parallel experiment between 1a and 1a-*d*$_5$:



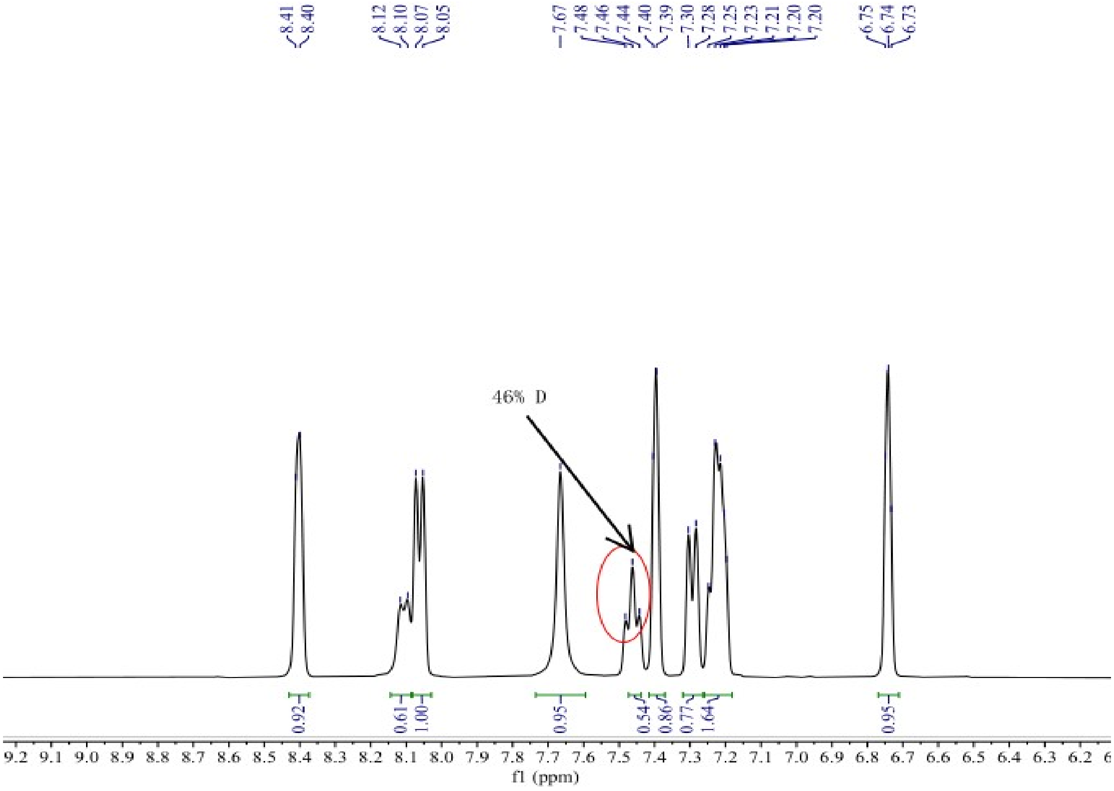
Two sets of parallel reactions of **1a** and **1a-*d*$_5$** (0.1 mmol) were subjected under both standard conditions. The reaction was allowed to afford **3aa** (91%) or **3aa-*d*$_4$** (88 %), **4aa** (67 %) or **4aa-*d*$_4$** (23 %), The kinetic isotope effect (k_H/k_D) value was determined as 1.02 and 2.90, respectively.

Procedure for competition experiment between 1a and 1a-*d*$_5$:

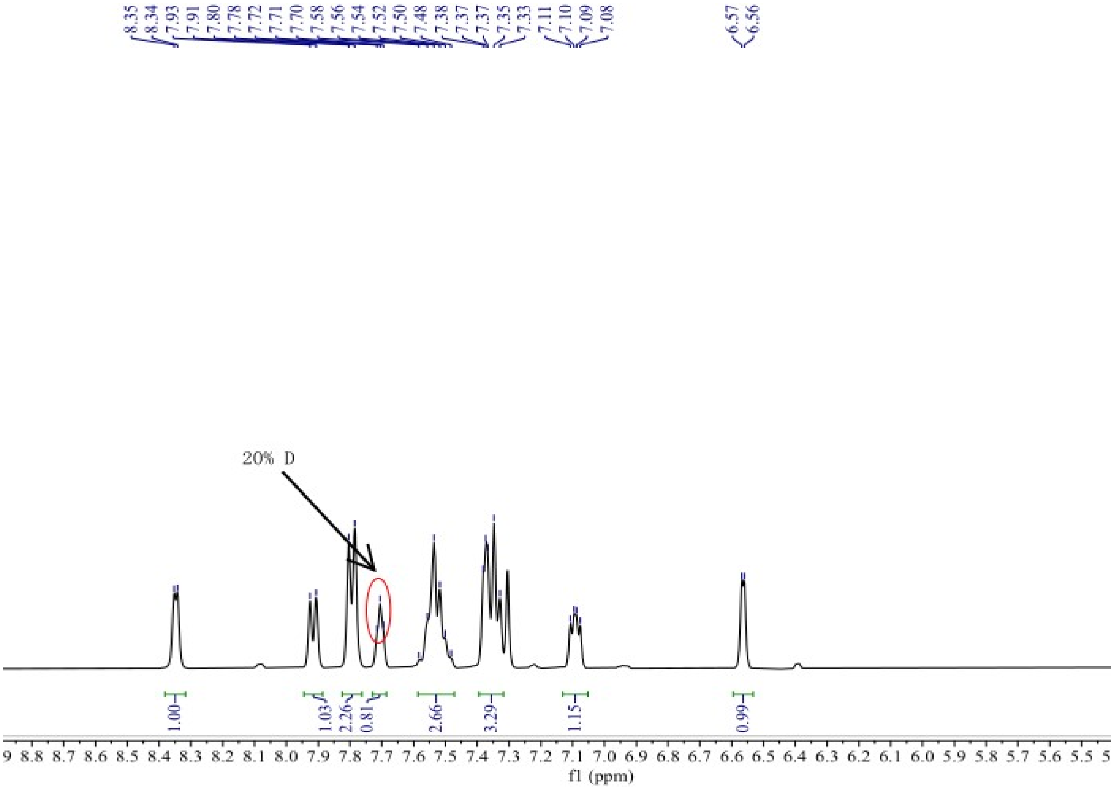


To a solution of benzoyloxycarbamate **2a** (28.4 mg, 1.2 equiv.) was added 0.1 mmol of **1a** and o.1 mmol **1a-*d*$_5$** under standard conditions, resulting in a mixture of **4aa** and **4aa-*d*$_4$** (23.4 mg), **3aa** and **3aa-*d*$_4$**(30.3 mg). The ratios of both products (**3aa**:**3aa-**d$_4$=1.2) and (**4aa**:**4aa**-d$_4$=4) were determined by ^{1}H NMR spectroscopy.

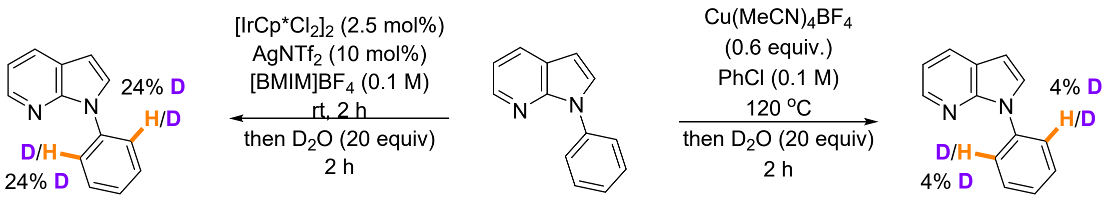
^{1}**H NMR** of **3aa** and **3aa-d$_4$**



^{1}**H NMR of 4aa and 4aa-d$_4$**



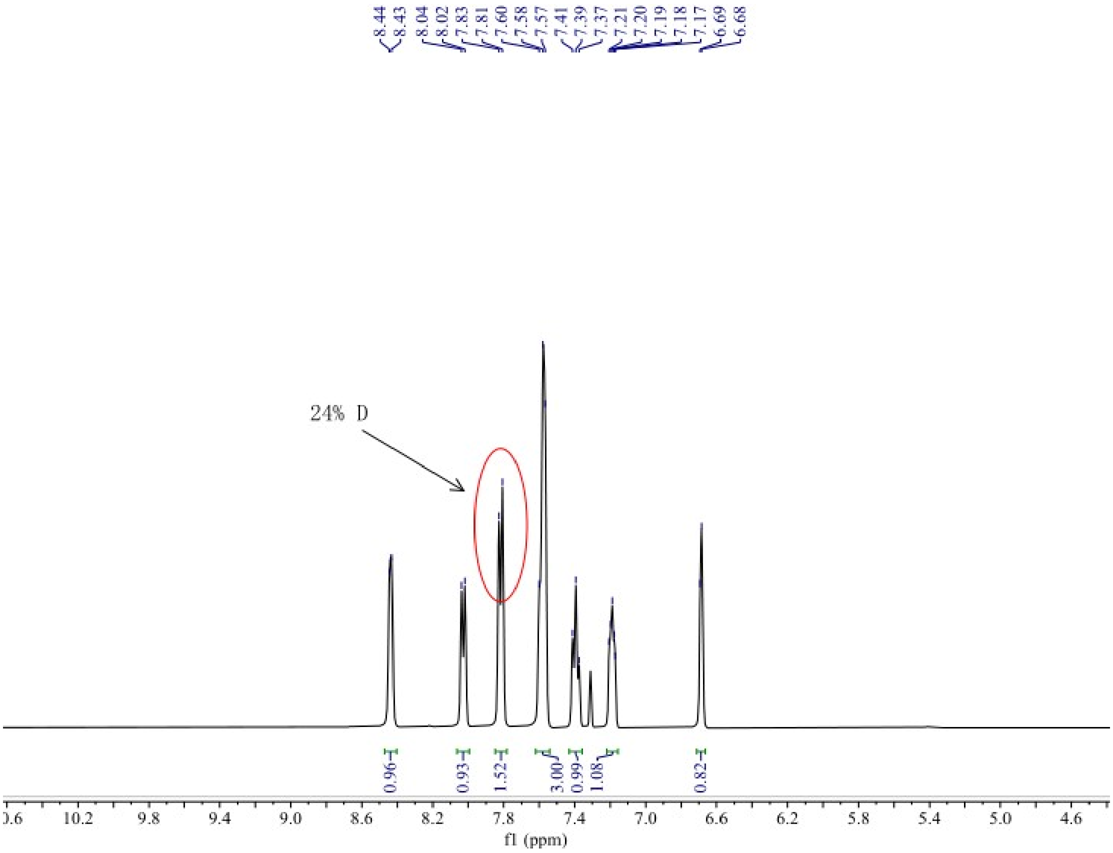
(c) H/D Exchange Experiment:



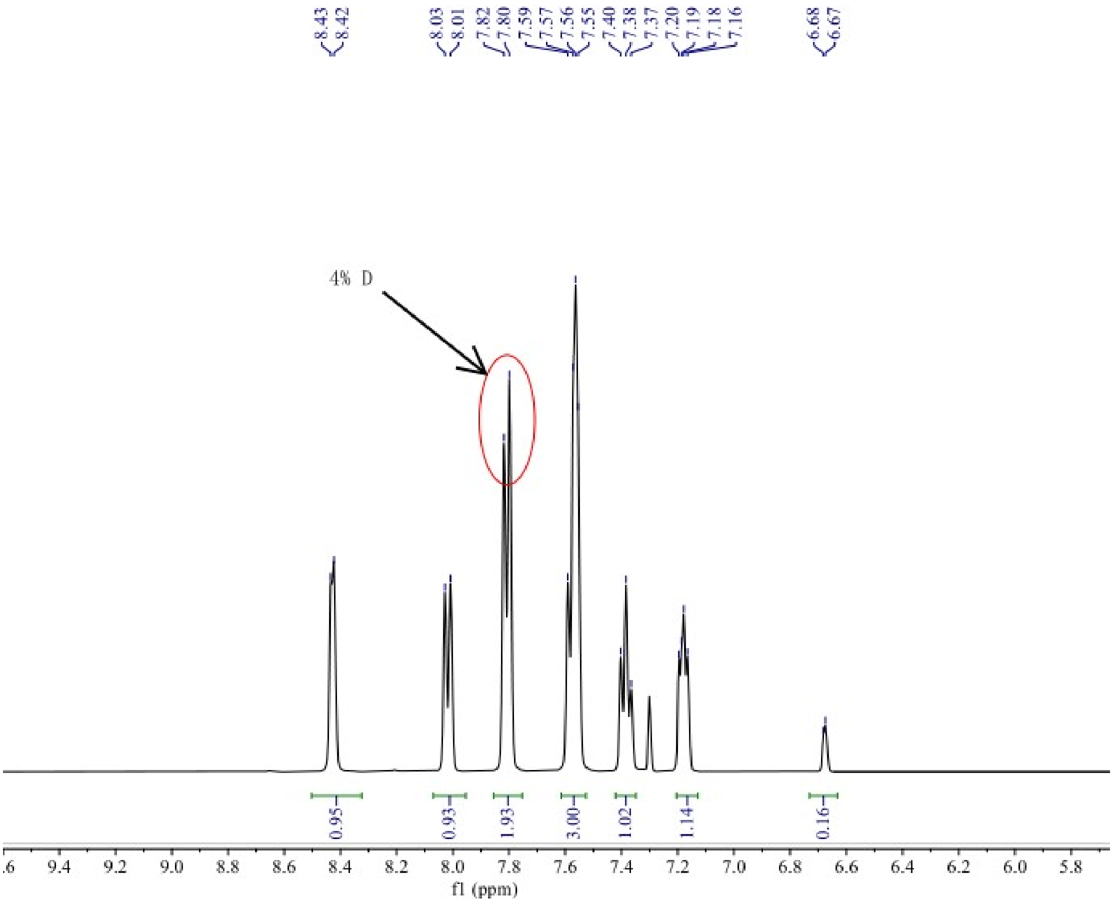
deuterio **1a** **1a** deuterio **1a**

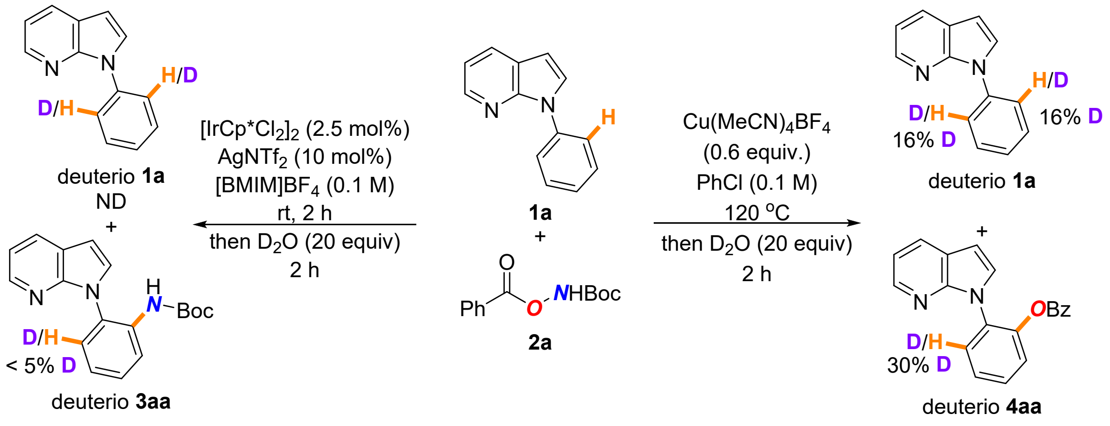
1a was subjected to each reaction conditions followed by addition of D_2O, 24% deuterium incorporation was observed by ^1H NMR analysis under iridium catalysis, whereas no deuterium incorporation was observed under copper system.

Under Iridium Catalysis



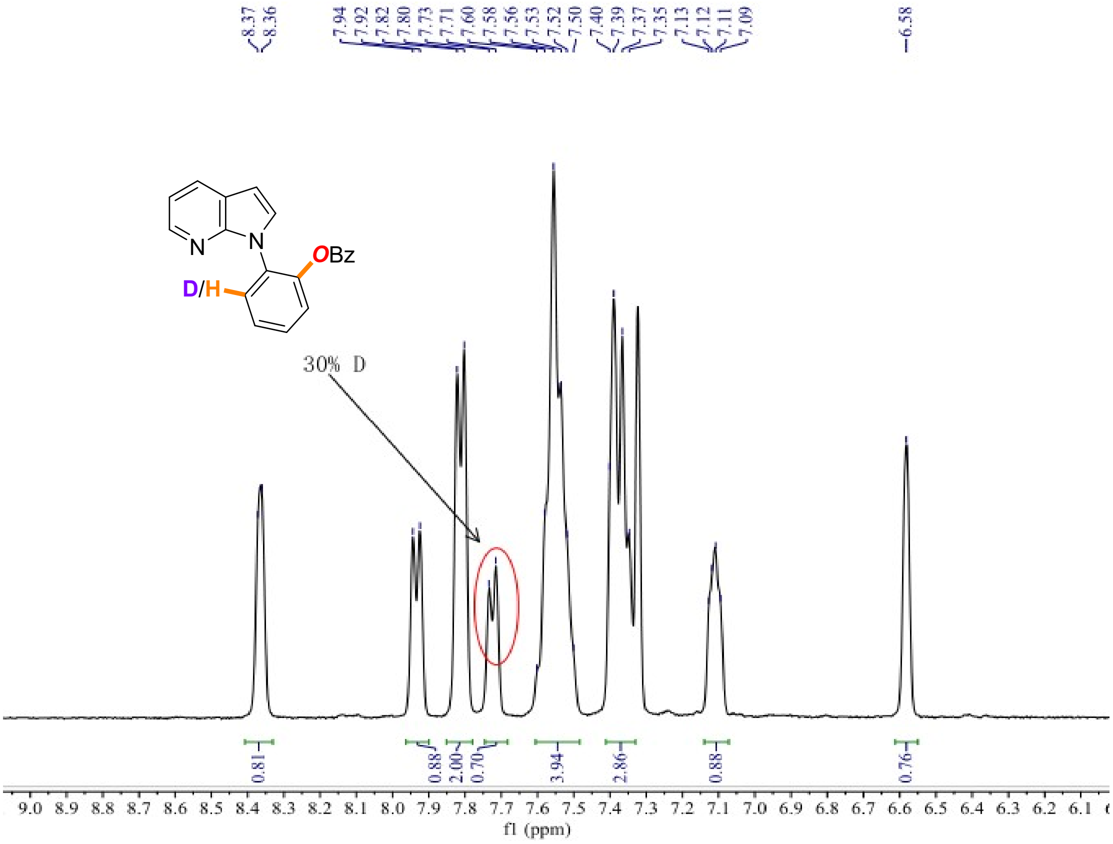
Under Copper System

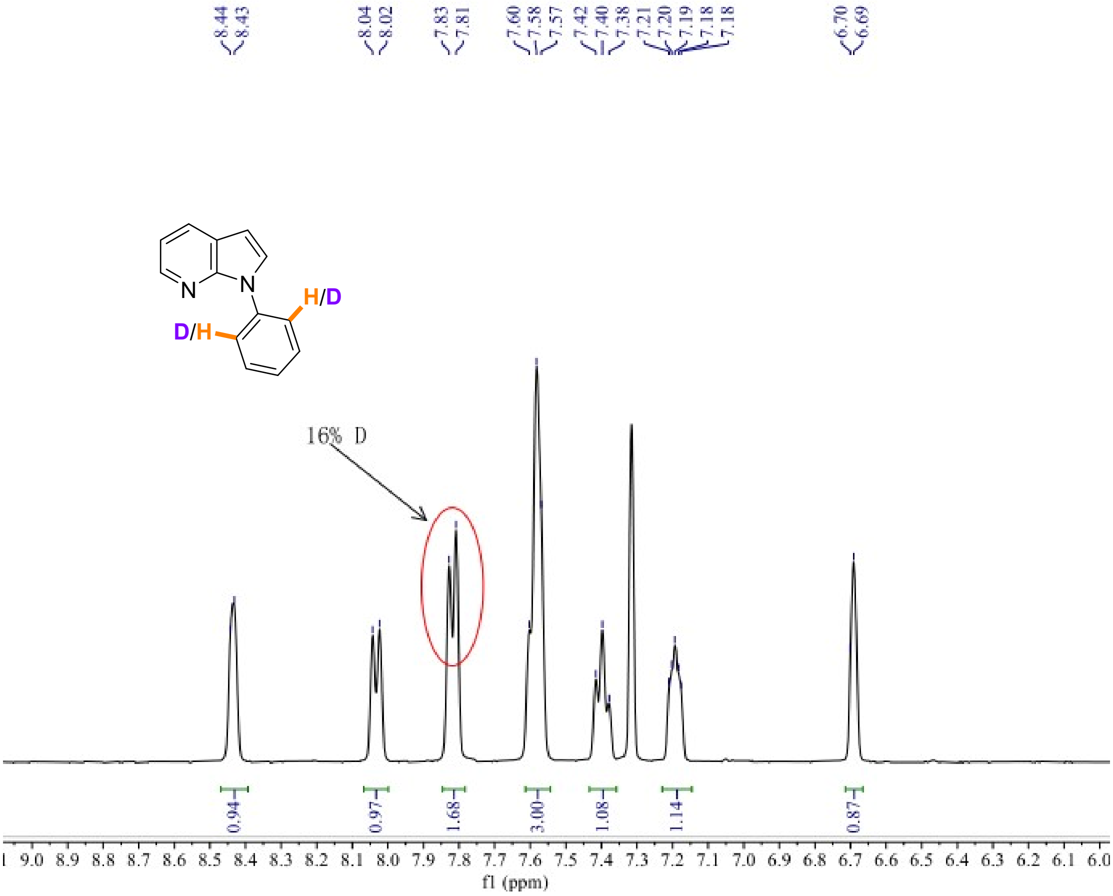




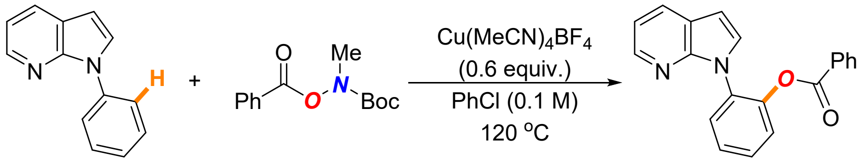
1a and **2a** were employed in each reaction conditions, subsequently D_2O was added to the reaction mixture. Under iridium catalysis, no **1a** was recovered and the reaction proceed with full conversion. Under copper system, large H/D scrambling was observed in the presence of **2a**.

Under Copper System





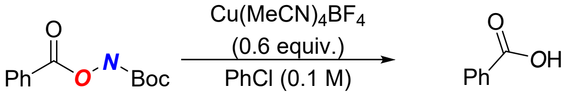
(d)



1a **2u** **4aa** (63%)

1a and **2u** were employed under standard conditions, the corresponding product was obtained in 63% yield.

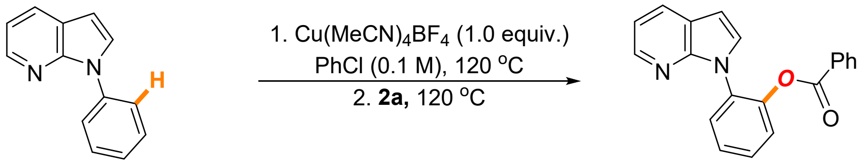
(e)



2a trace

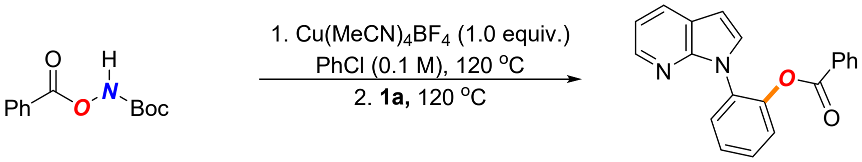
2a was subjected in the standard conditions, no **2a** was observed and it underwent decomposed after 5 h. However, only trace amount of benzoic acid was detected.

(f)



1a **4aa** N.D.

1a was subjected in the standard reaction condition for 12 h, then **2a** was added and the reaction mixture was stirred at 120 °C for 12 h, **4aa** was not detected.



(g) **2a** **4aa** (75%)

2a was subjected in the standard reaction condition for 12 h, then **1a** was added and the reaction mixture was stirred at 120 °C for 12 h, **4aa** was obtained in 75% yield.

8 X-Ray Crystal Data of Compound 6aa

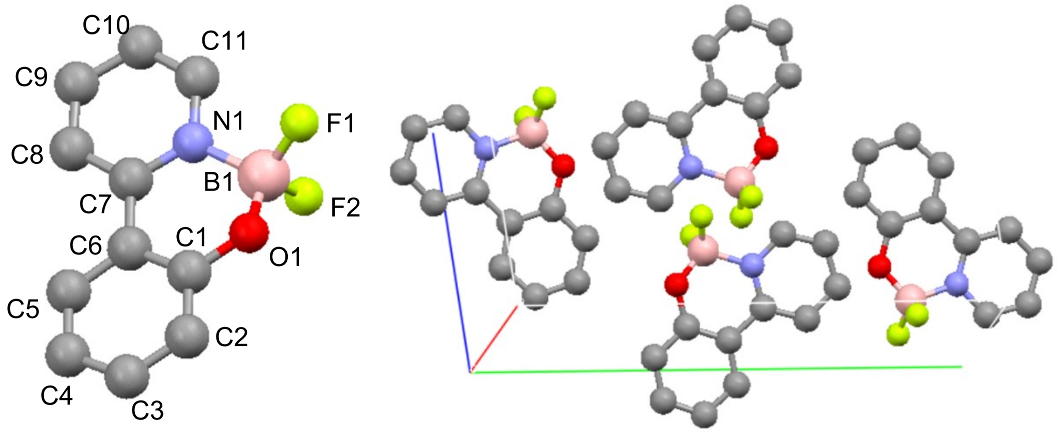


Figure S1 Crystal structure and packing mode **6aa**

Table S2 Crystal data and structure refinement

Identification code	1
Empirical formula	$C_{11}H_8BF_2NO$
Formula weight	218.99
Temperature/K	273(2)
Crystal system	monoclinic
Space group	$P\ 2_1/c$
a/Å	7.4288(4)
b/Å	15.5325(8)
c/Å	8.9822(4)
α/°	90
β/°	108.6544(16)
γ/°	90
Volume/Å^3	981.988
Z	4
Z’	0
R-factor	6.34
ρ_{calc}g/cm^3	1.481
F(000)	448
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.623 to 27.533
Index ranges	$-9 \le h \le 9$, $-20 \le k \le 20$, $-11 \le l \le 11$
Reflections number	29116
Reflns/restraints/parameters	2263/0/146
S	0.998

Table S3 Bond lengths [Å].

Atom	Atom	Length/Å	Atom	Atom	Length/Å
B1	F1	1.383	C5	H5	0.93
B1	F2	1.377	C5	C6	1.401
B1	N1	1.588	C6	C7	1.461
B1	O1	1.417	C7	C8	1.392
C1	C2	1.393	C7	N1	1.358
C1	C6	1.398	C8	H8	0.93
C1	O1	1.349	C8	C9	1.366
C2	H2	0.93	C9	H9	0.93
C2	C3	1.357	C9	C10	1.381
C3	H3	0.93	C10	H10	0.93
C3	C4	1.379	C10	C11	1.361
C4	H4	0.93	C11	H11	0.93
C4	C5	1.373	C11	N1	1.353

Table S4 Bond angles [°].

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
F2	B1	F1	109.18(16)	C1	C6	C7	120.28(15)
F2	B1	O1	109.55(18)	C5	C6	C7	121.86(17)
F1	B1	O1	112.81(19)	N1	C7	C8	118.33(16)
F2	B1	N1	108.10(17)	N1	C7	C6	117.67(15)
F1	B1	N1	105.97(17)	C8	C7	C6	123.98(16)
O1	B1	N1	111.07(15)	C9	C8	C7	120.9(2)
O1	C1	C2	117.67(18)	C8	C9	C10	119.7(2)
O1	C1	C6	121.88(16)	C11	C10	C9	118.50(18)
C2	C1	C6	120.36(18)	N1	C11	C10	122.04(19)
C3	C2	C1	120.2(2)	C11	N1	C7	120.55(16)
C2	C3	C4	120.7(2)	C11	N1	B1	117.57(15)
C5	C4	C3	119.8(2)	C7	N1	B1	121.73(15)
C4	C5	C6	121.0(2)	C1	O1	B1	122.61(15)
C1	C6	C5	117.84(17)				

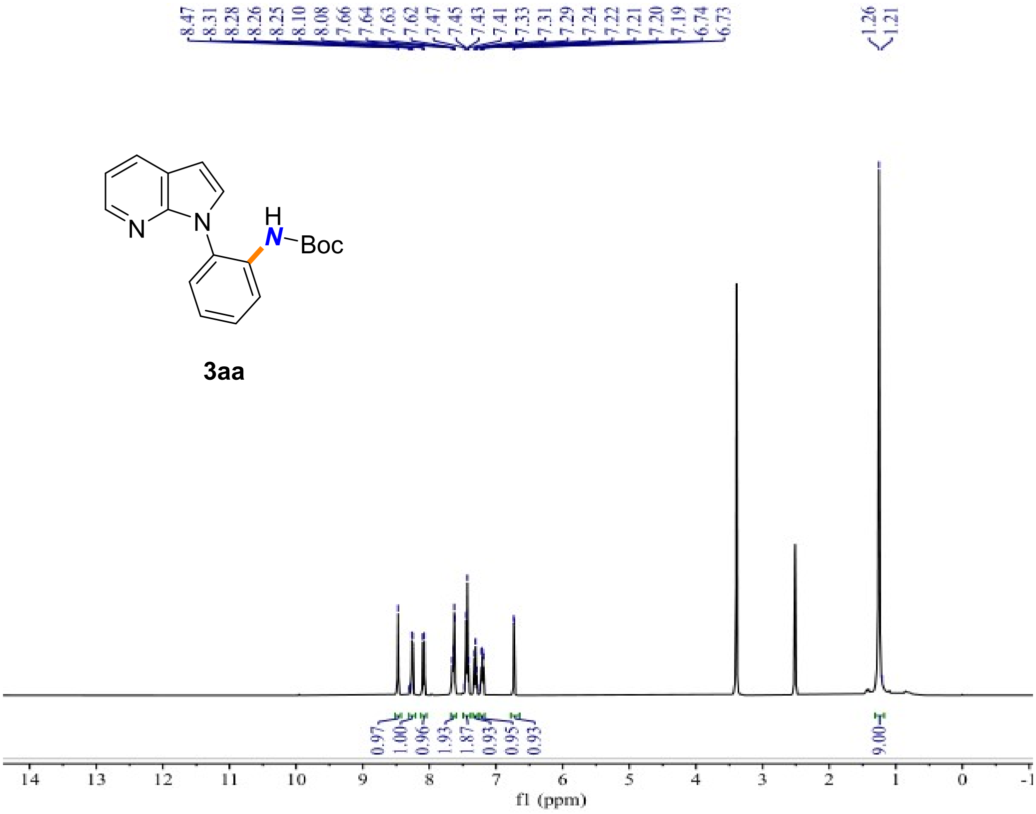
9 References and Notes

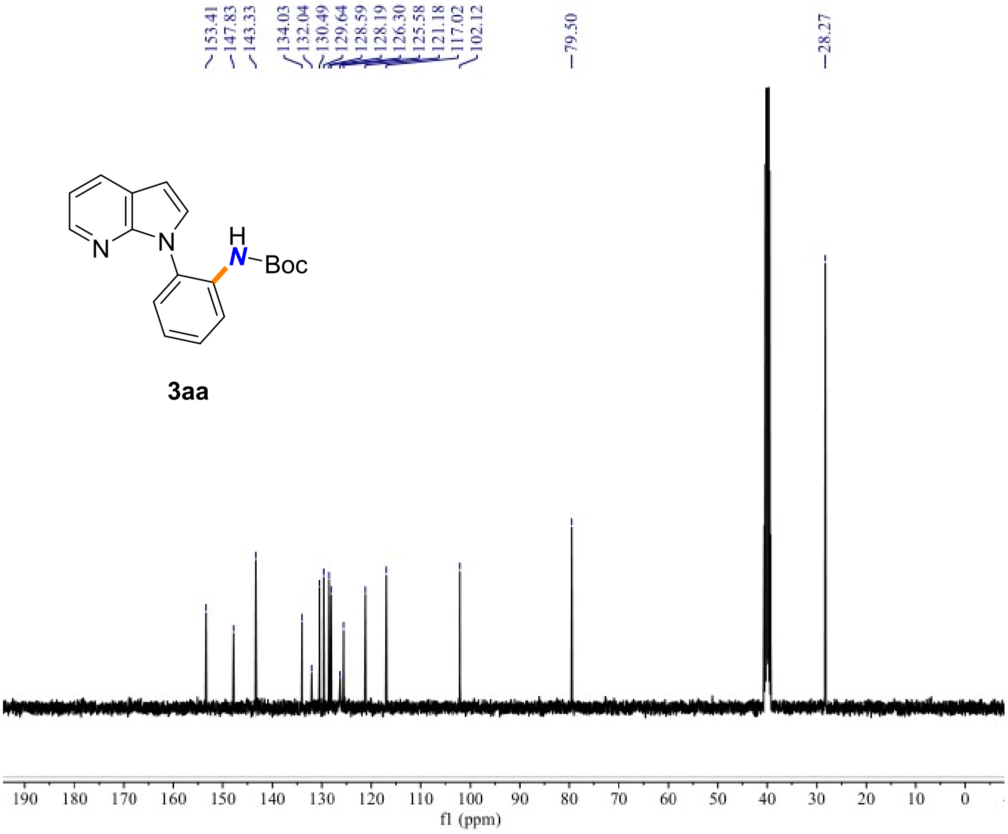
[S1] G. Qian, X. Hong, B. Liu, H. Mao, B. Xu, Rhodium-Catalyzed Regioselective C–H Chlorination of 7-Azaindoles Using 1,2-Dichloroethane, *Org. Lett*. **2014**, *16*, 5294–5297.

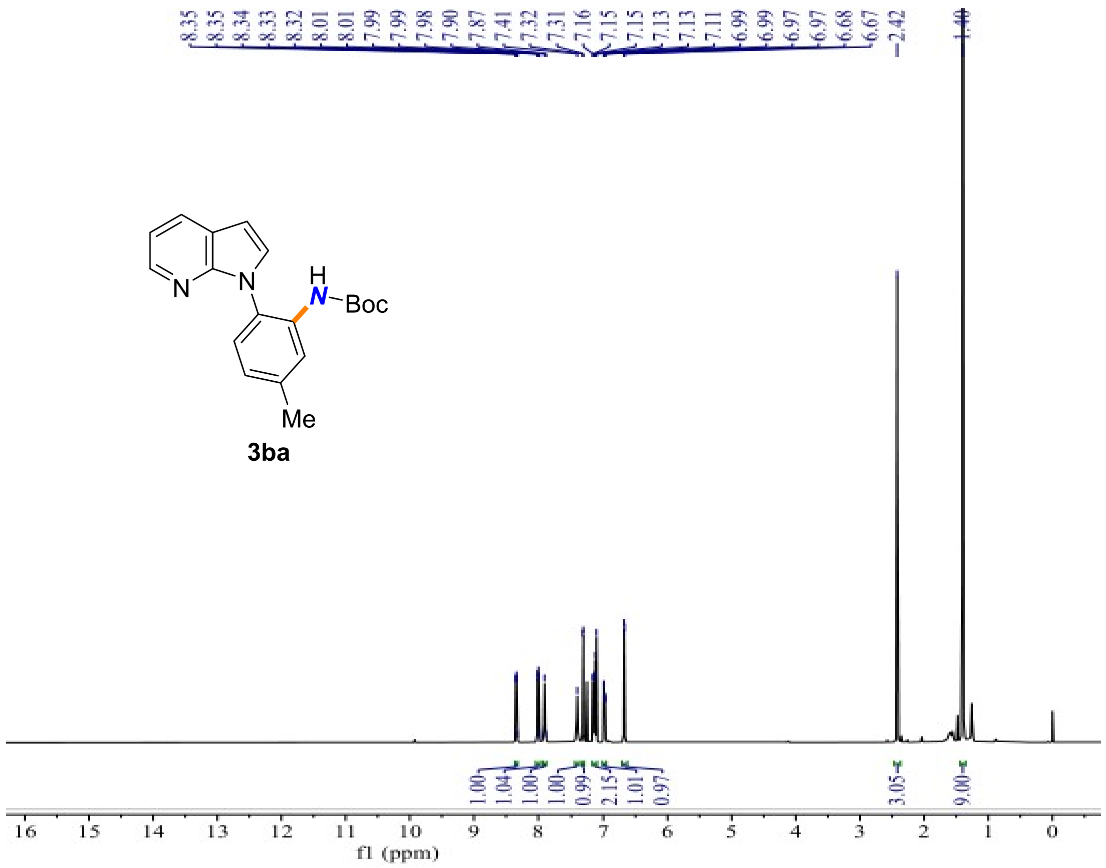
[S2] J. Jinwon, L. Changseok, S. Huiyeong, H. Sungwoo, NiH-Catalyzed Proximal-Selective Hydroamination of Unactivated Alkenes. *J. Am. Chem. Soc.* **2020**, *142*, 20470–20480.

[S3] C. S. Beshara, A. Hall, R. L. Jenkins, K. L. Jones, T. C. Jones, N. M. Killeen, P. H. Taylor, S. P. Thomas, N. C. O. Tomkinson, A general method for the alpha-acyloxylation of carbonyl compounds, *Org. Lett.* **2005**, *7*, 5729–5732.

10 Copies of NMR Spectra of the All Compounds



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7.98
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7.41
7.32
7.31
7.16
7.15
7.15
7.13
7.13
7.11
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6.99
6.97
6.97
6.68
6.67
2.42
1.40
N
N
H
N
Boc
Me
1.00
1.04
1.00
1.00
0.99
2.15
1.01
0.97
3.05
9.00
16
15
14
13
12
11
10
9
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4
3
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f1 (ppm)

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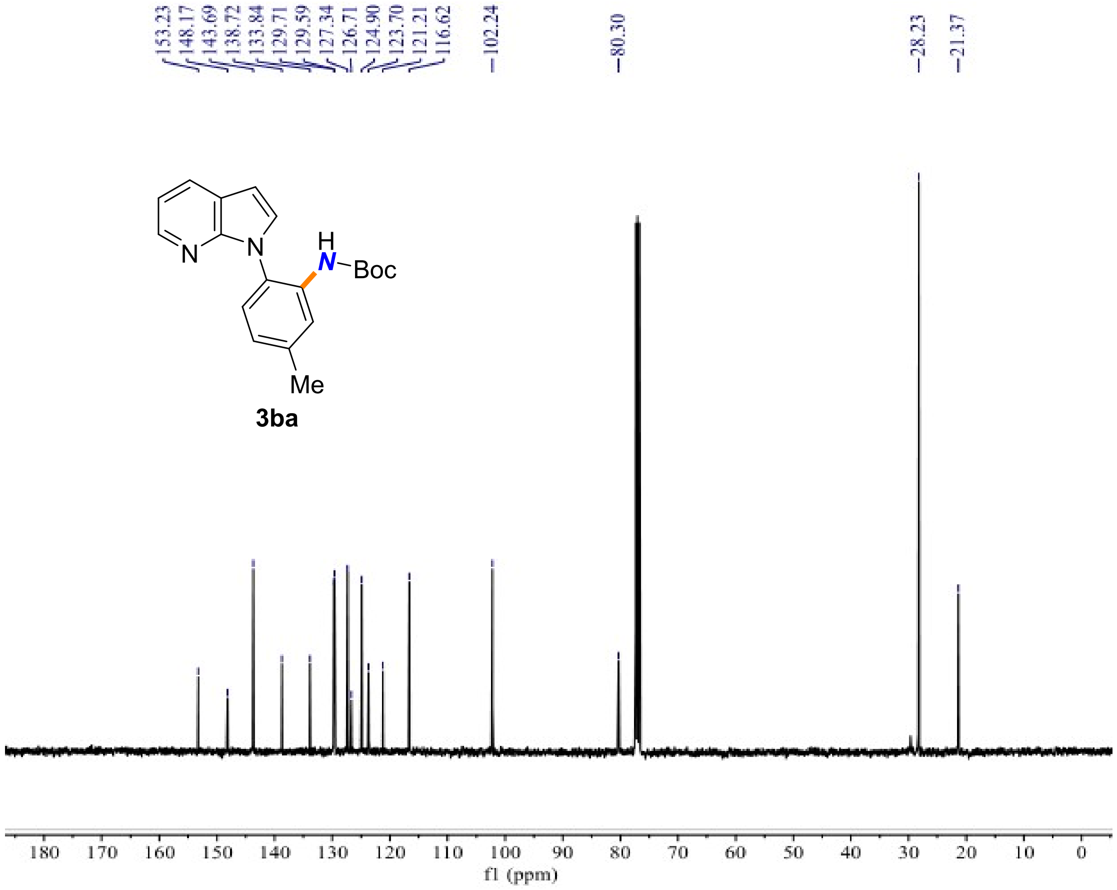
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80.30
28.23
21.37
N
N
H
N
Boc
Me
180
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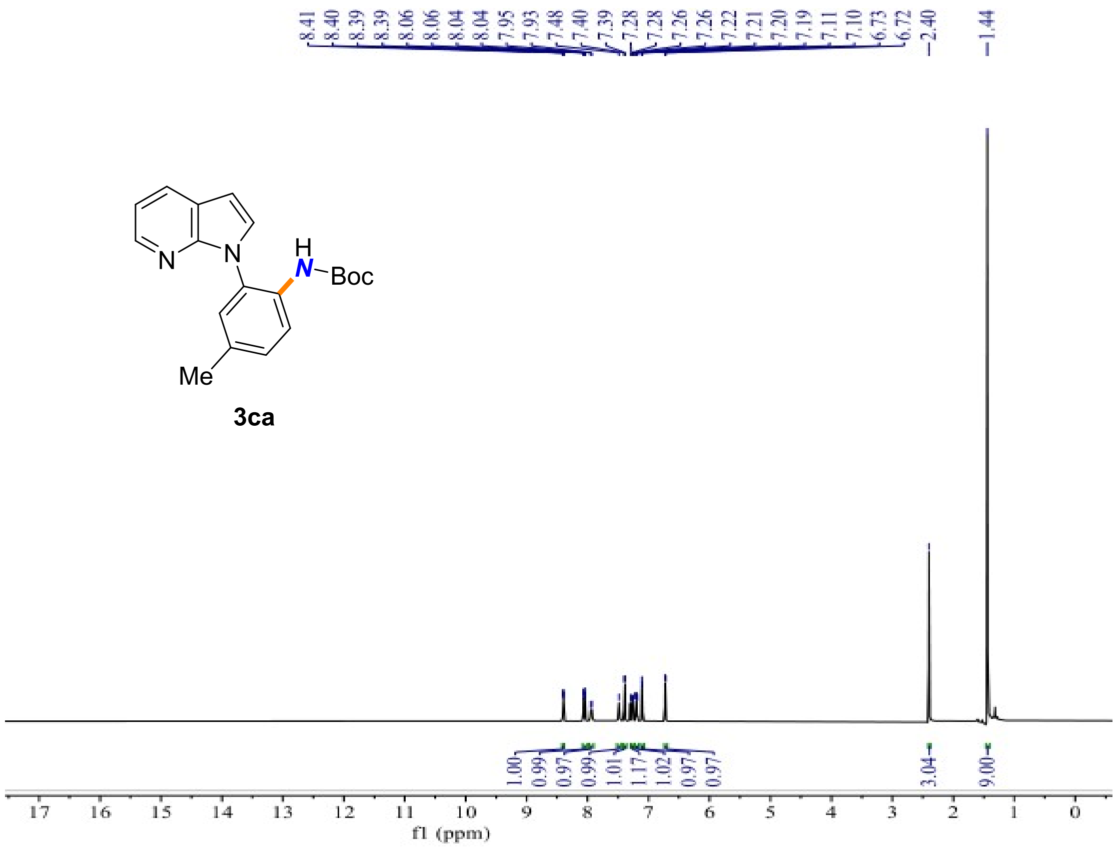
f1 (ppm)

3ba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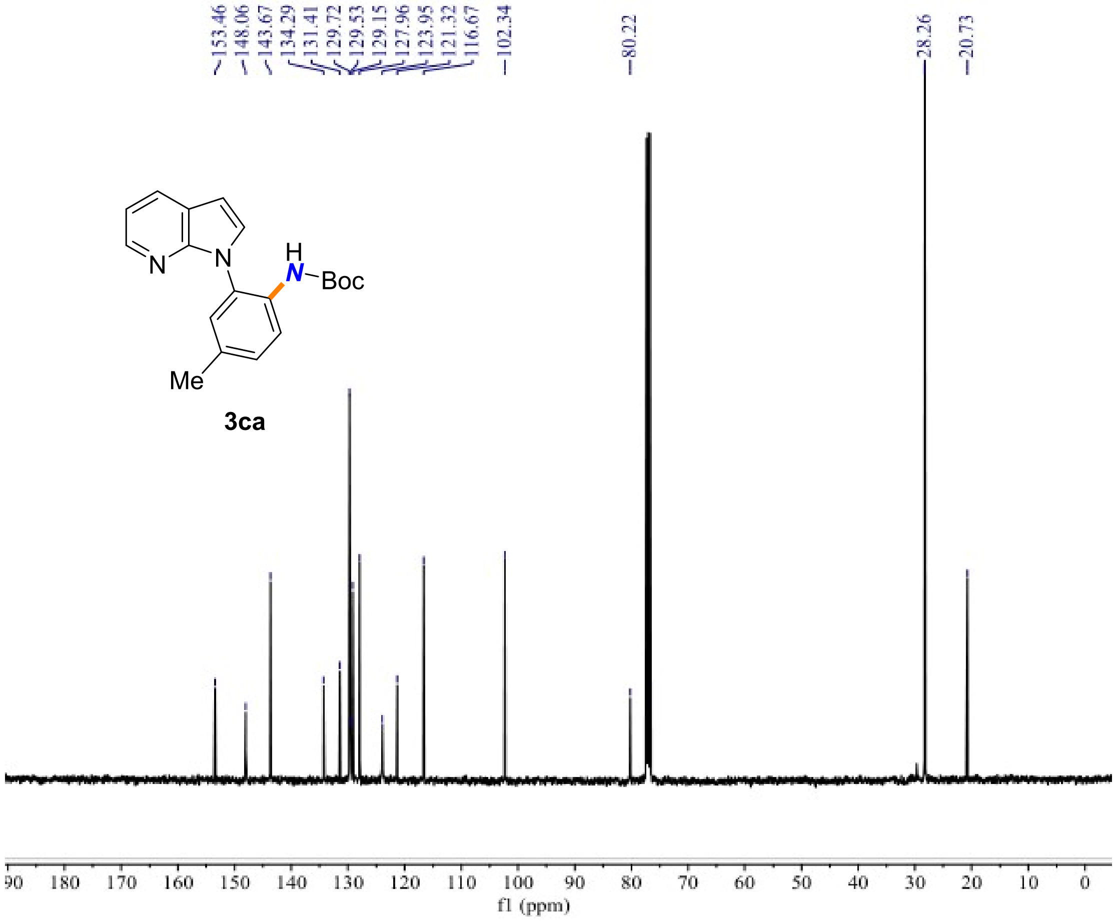
f1 (ppm)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102.34
80.22
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Boc
Me
3ca
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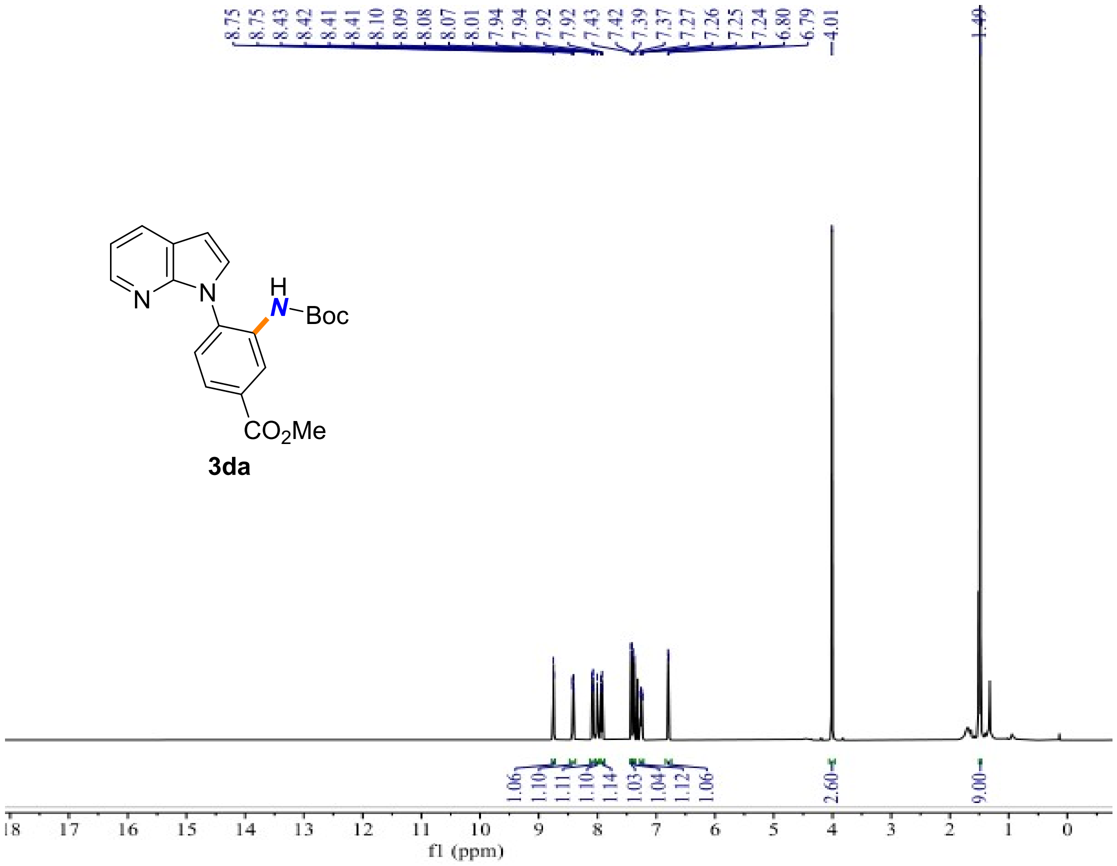
f1 (ppm)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7.42
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6.79
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Boc
CO_2Me
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1.10
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1.10
1.14
1.03
1.04
1.12
1.06
2.60
9.00
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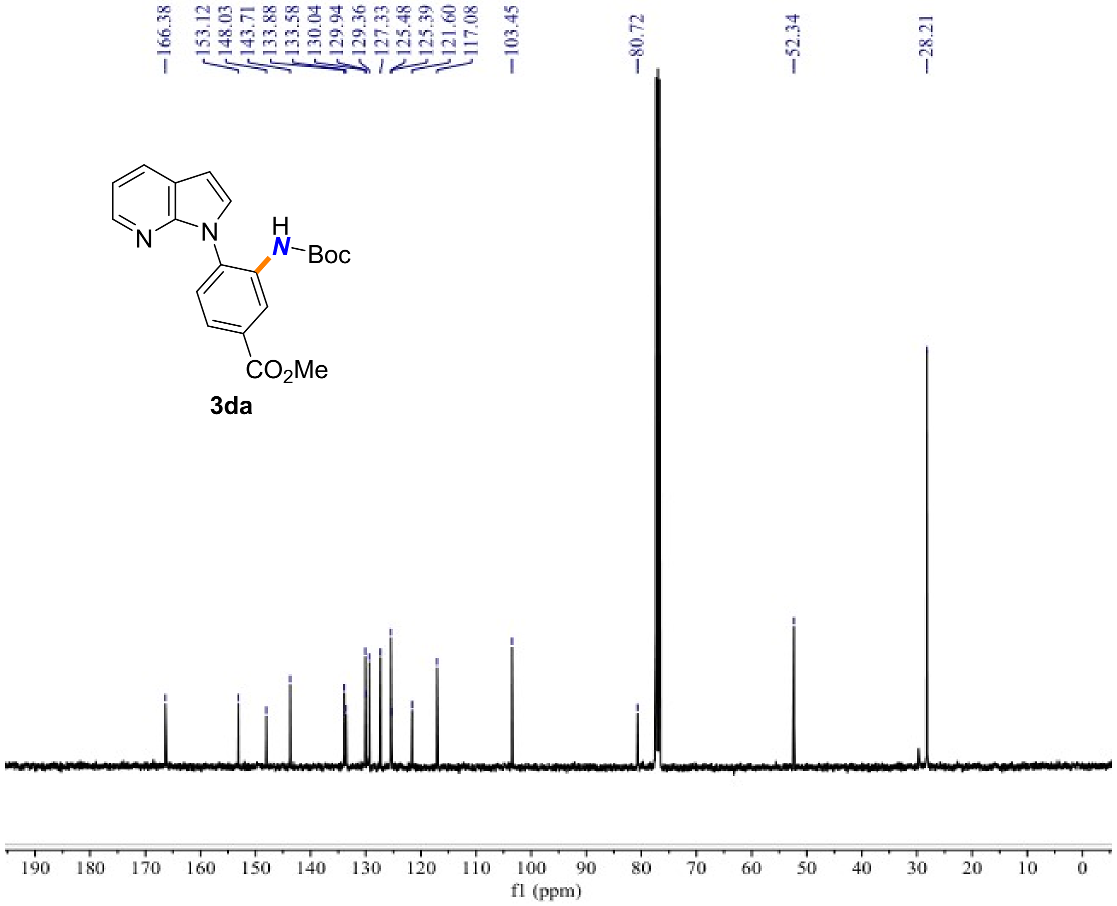
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CO_2Me
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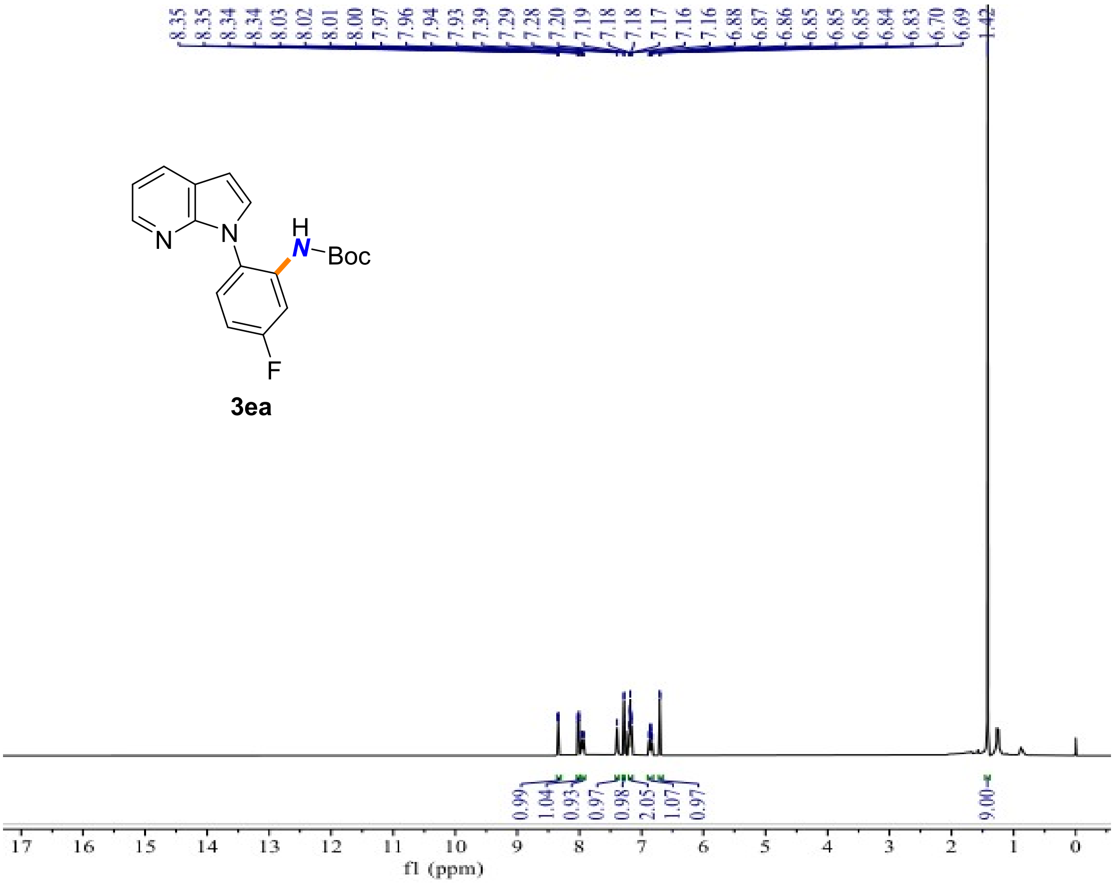
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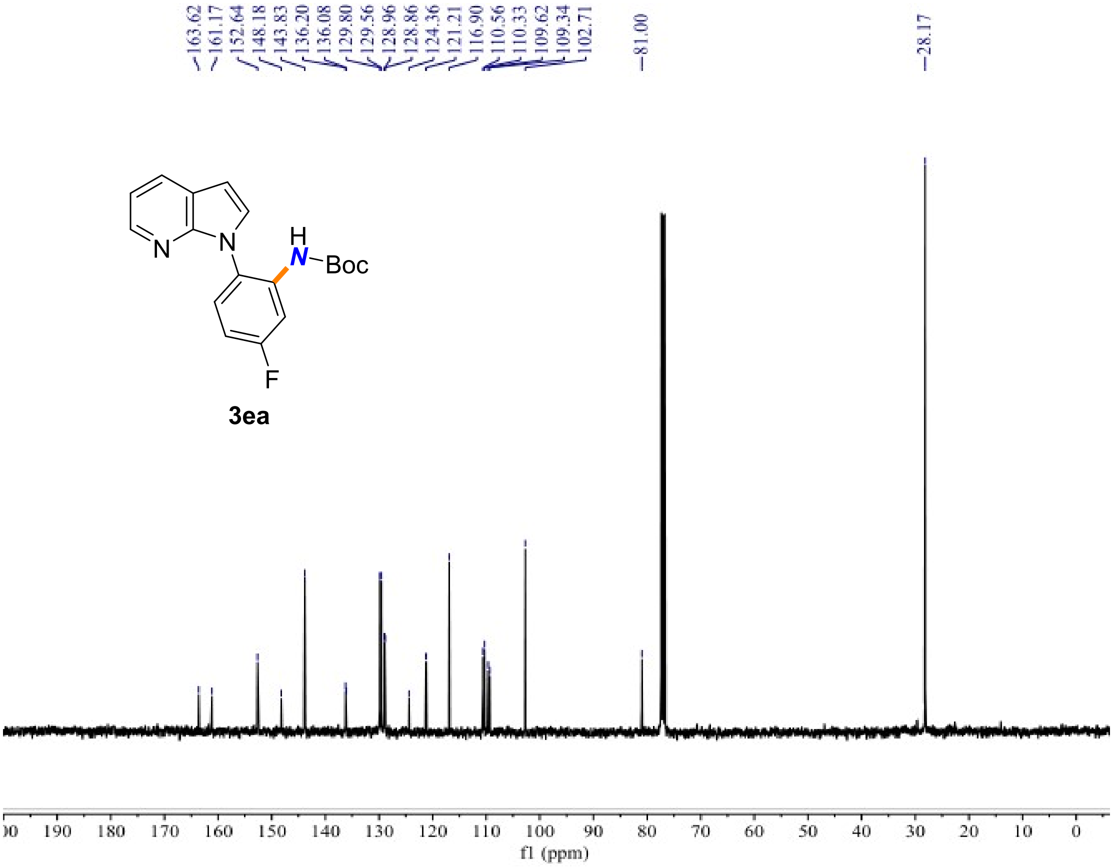
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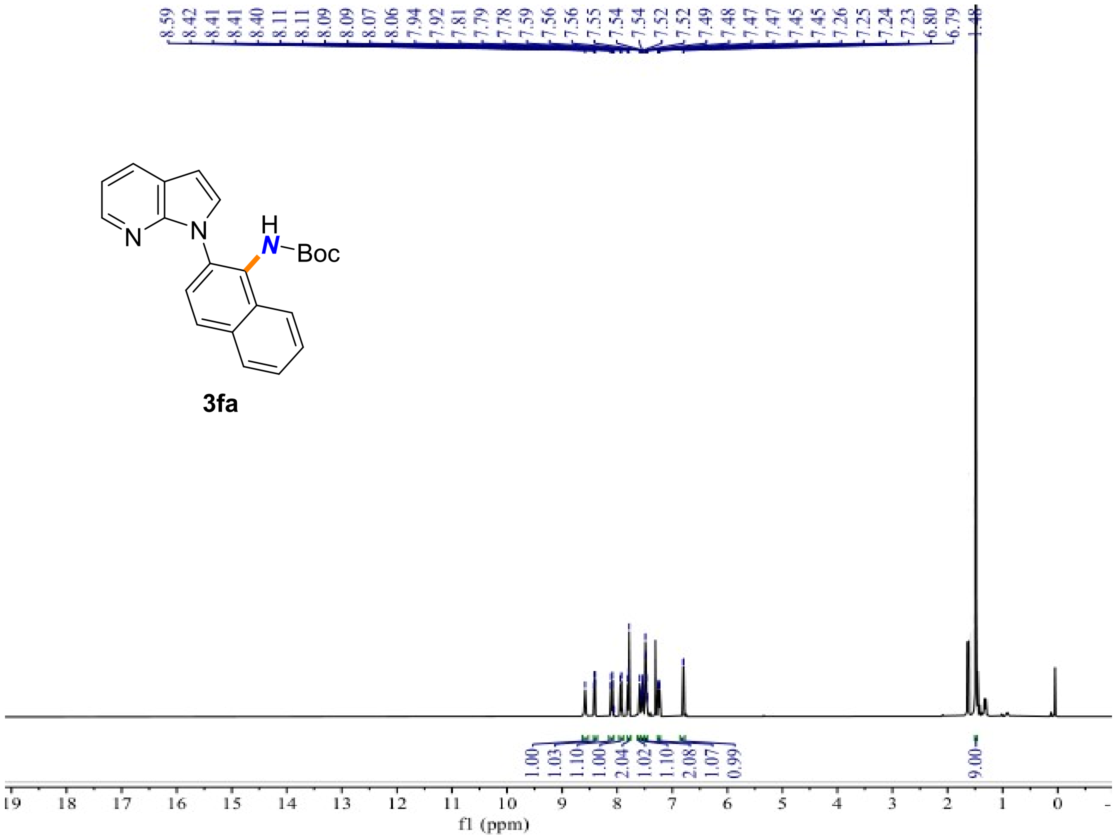
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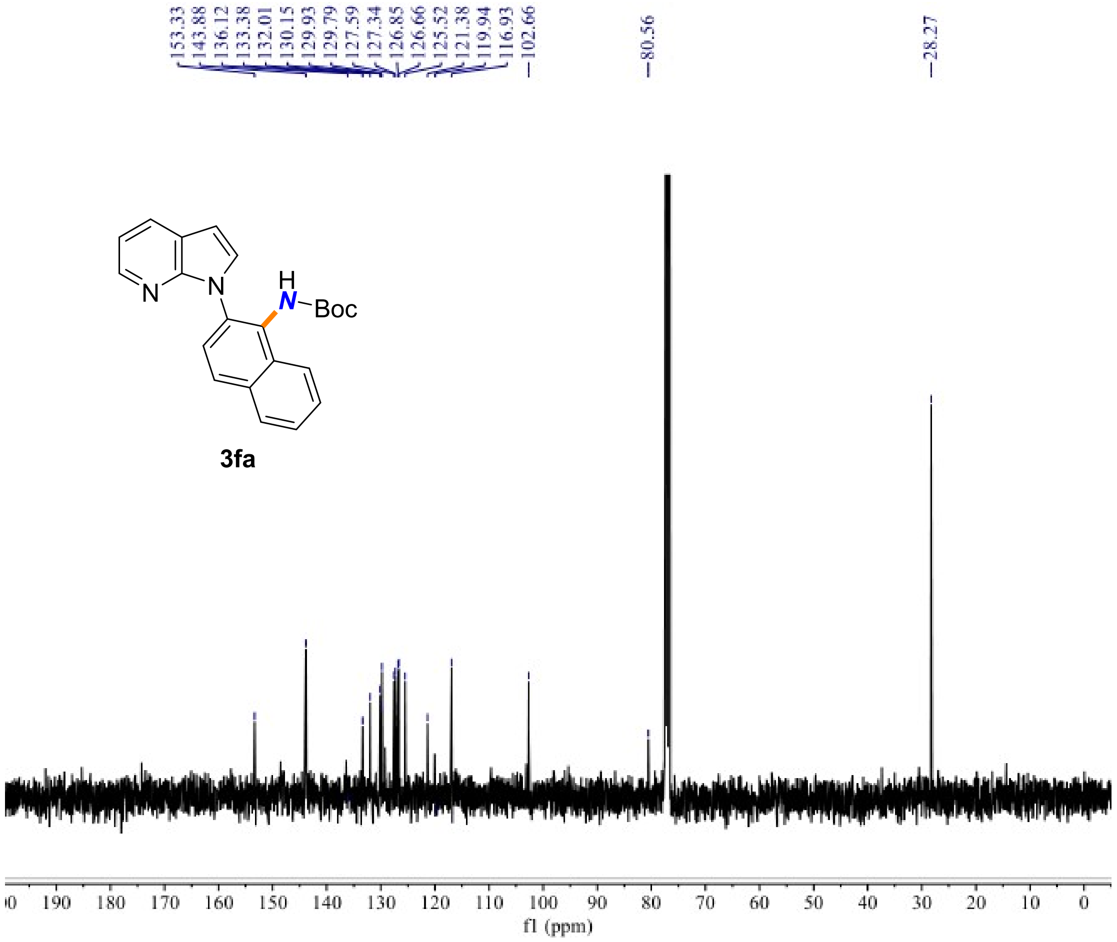
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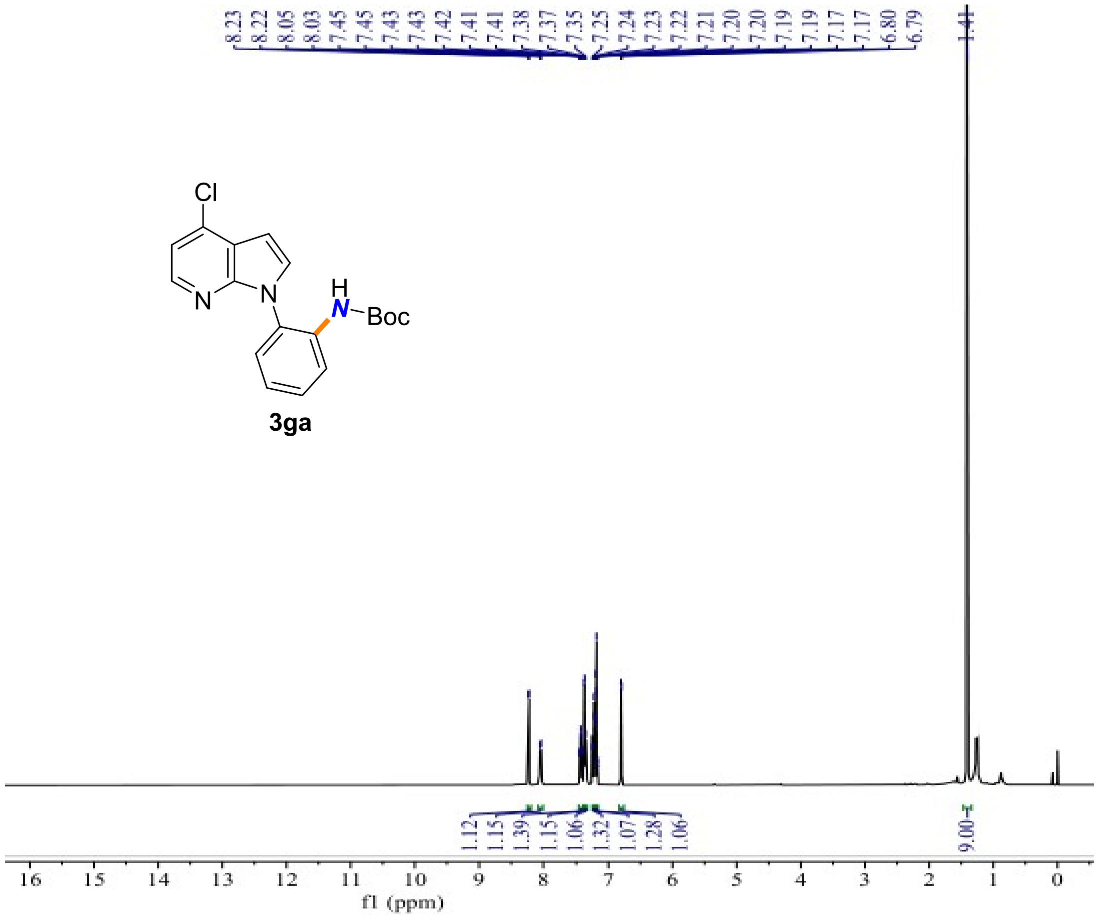
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7.20
7.19
7.19
7.17
7.17
7.17
6.80
6.79
1.41
Cl
N
N
H
N
Boc
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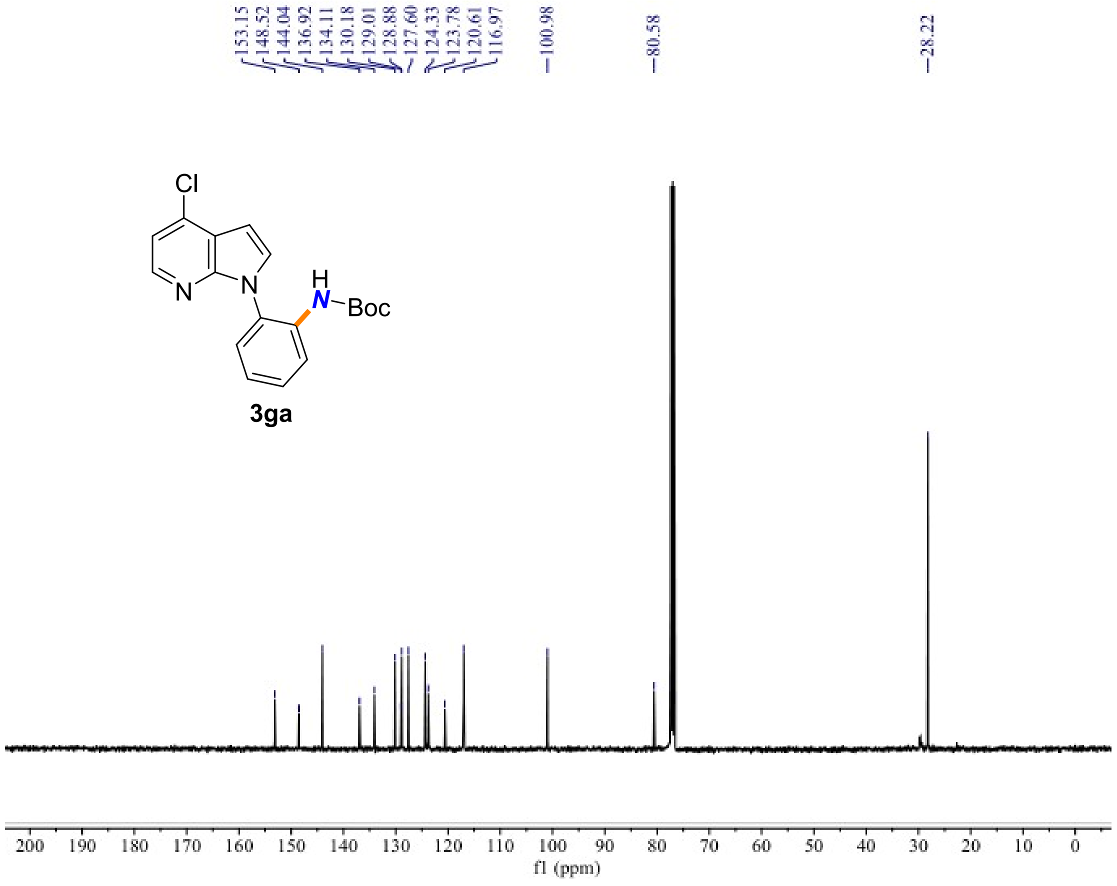
f1 (ppm)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100.98
80.58
28.22
Cl
N
N
H
N
Boc
3ga
200
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180
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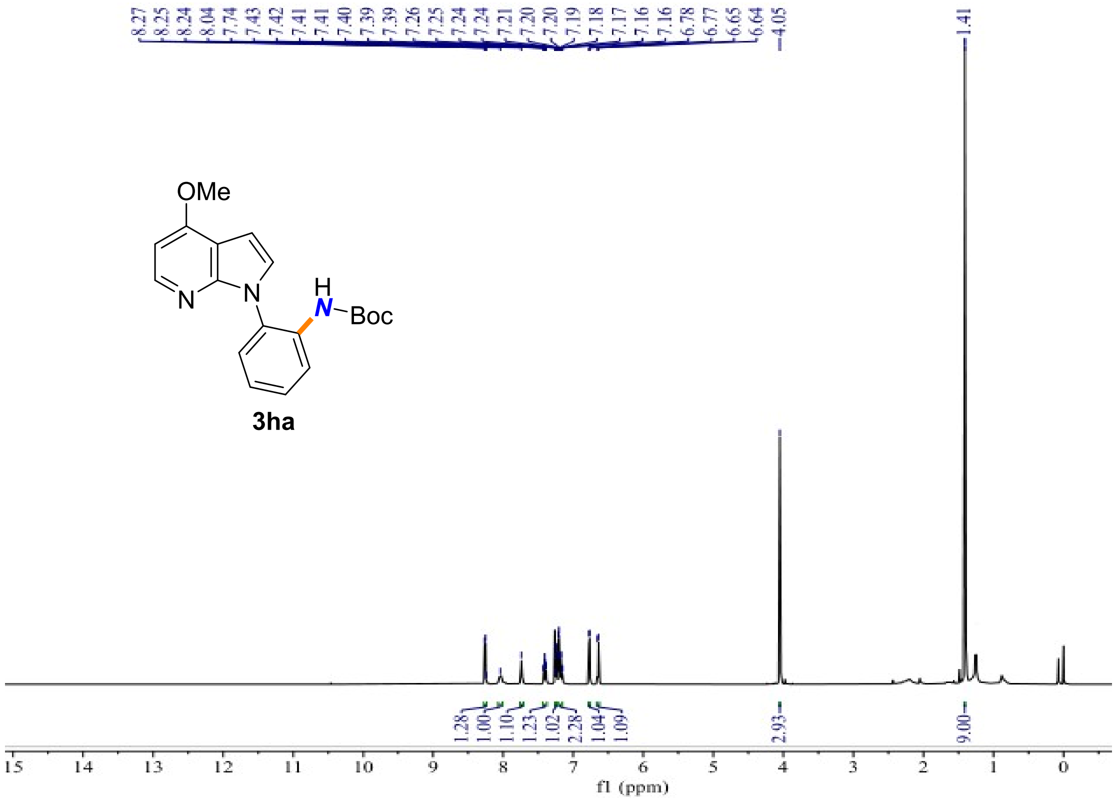
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7.25
7.24
7.24
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.16
6.78
6.77
6.65
6.64
4.05
1.41
OMe
N
N
H
N
Boc
3ha
1.28
1.00
1.10
1.23
1.02
2.28
1.04
1.09
2.93
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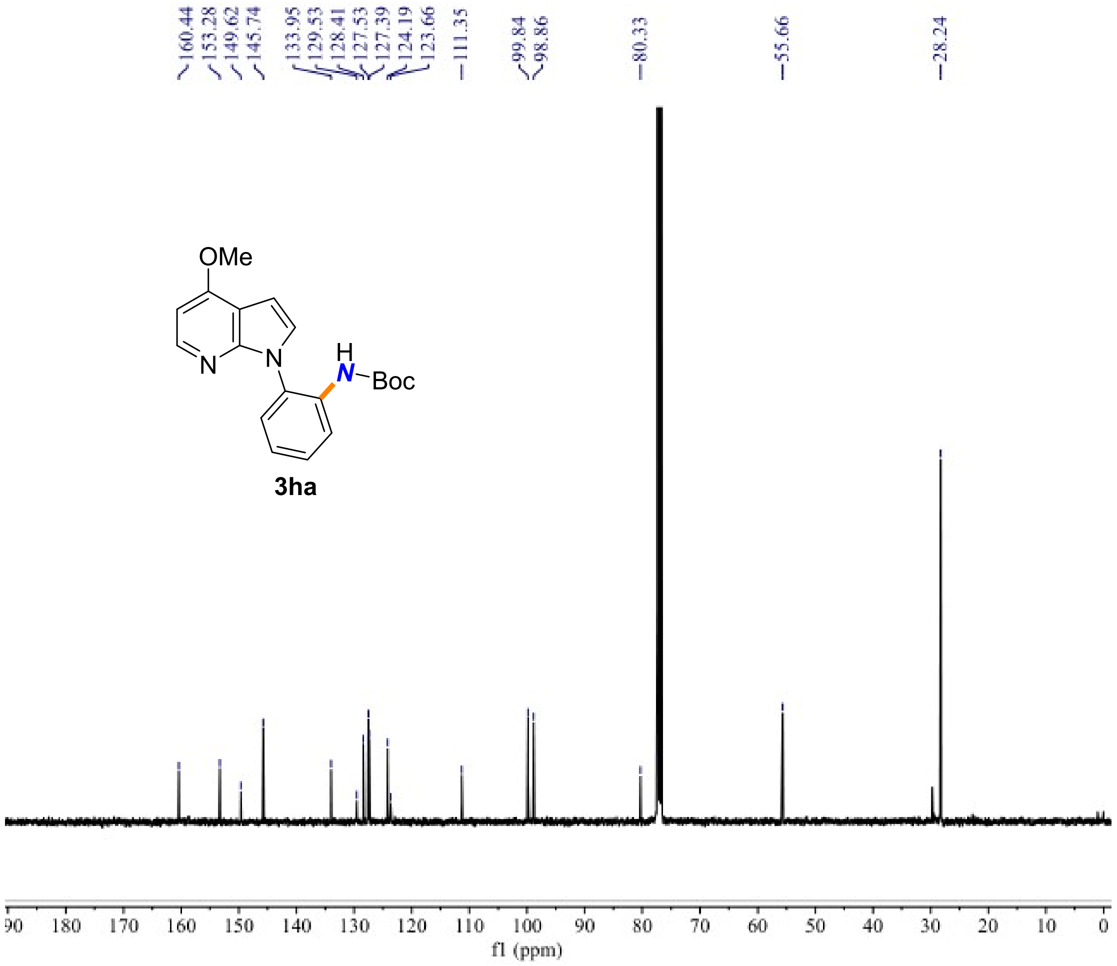
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99.84
98.86
80.33
55.66
28.24
OMe
N
N
H
N
Boc
3ha
190
180
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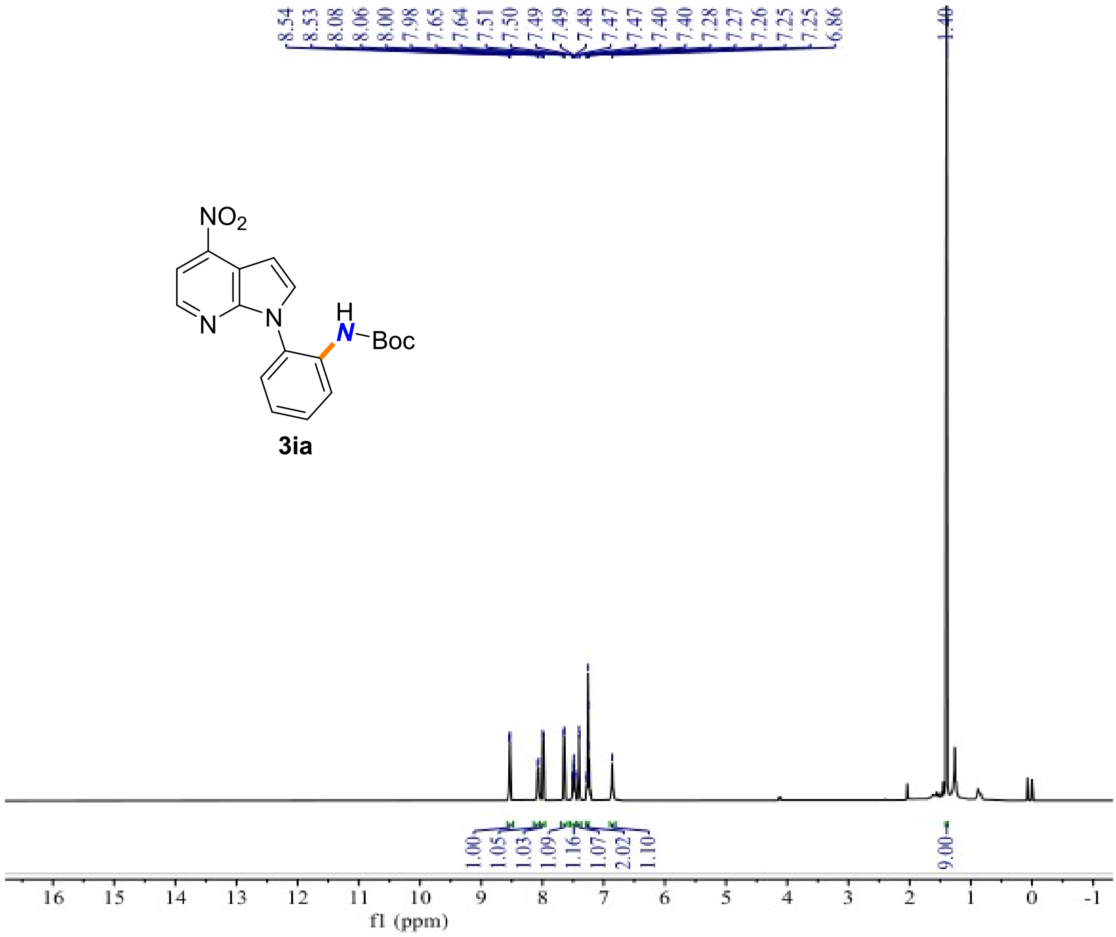
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7.47
7.47
7.40
7.40
7.28
7.27
7.26
7.25
7.25
6.86
1.40
NO2
N
N
H
N
Boc
3ia
1.00
1.05
1.03
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1.07
2.02
1.10
9.00
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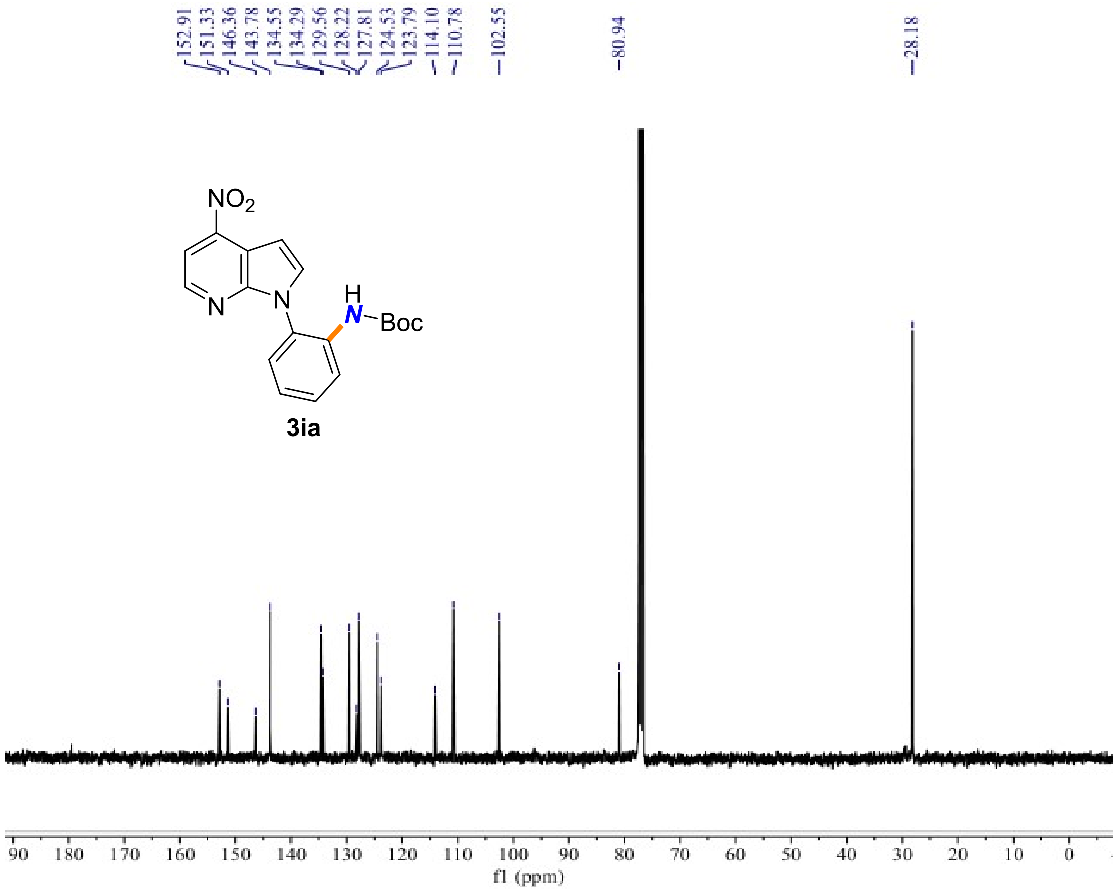
f1 (ppm)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123.79
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110.78
102.55
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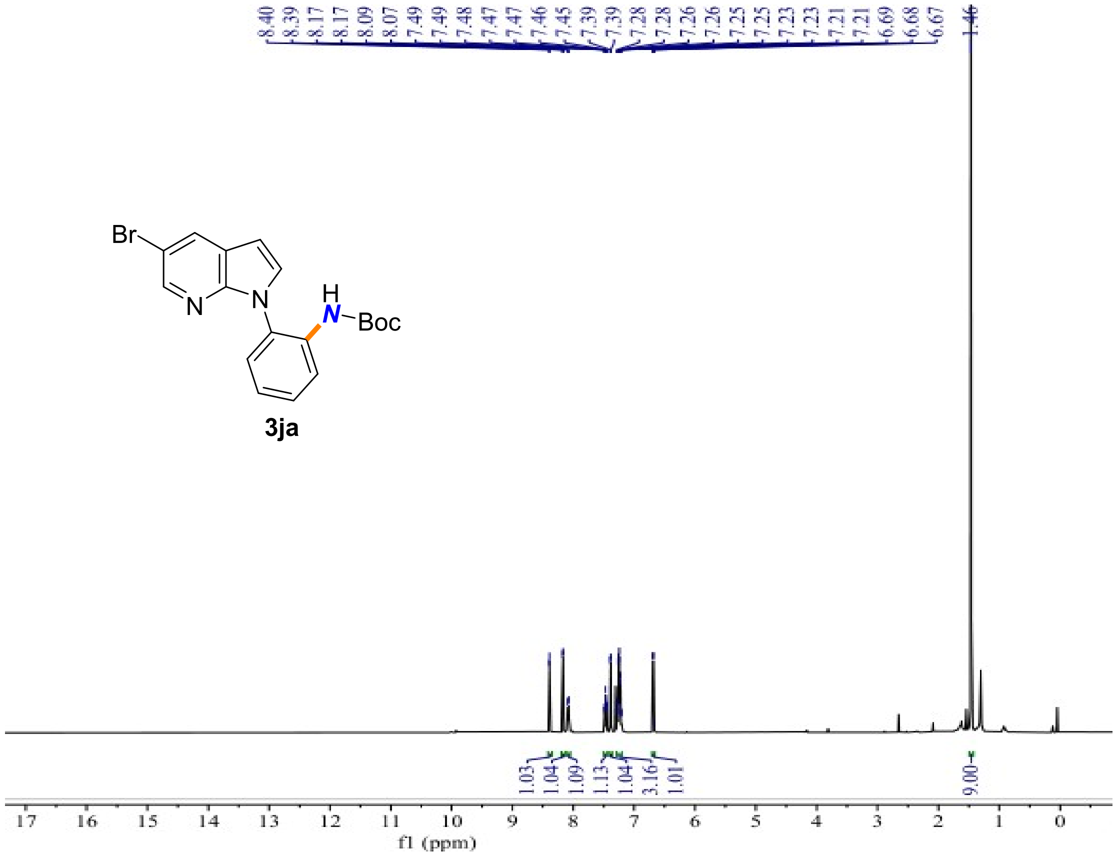
H
N
Boc
3ia
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.28
7.26
7.26
7.25
7.25
7.23
7.23
7.21
7.21
6.69
6.68
6.67
1.46
Br
N
N
H
N
Boc
1.03
1.04
1.09
1.13
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3.16
1.01
9.00
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f1 (ppm)

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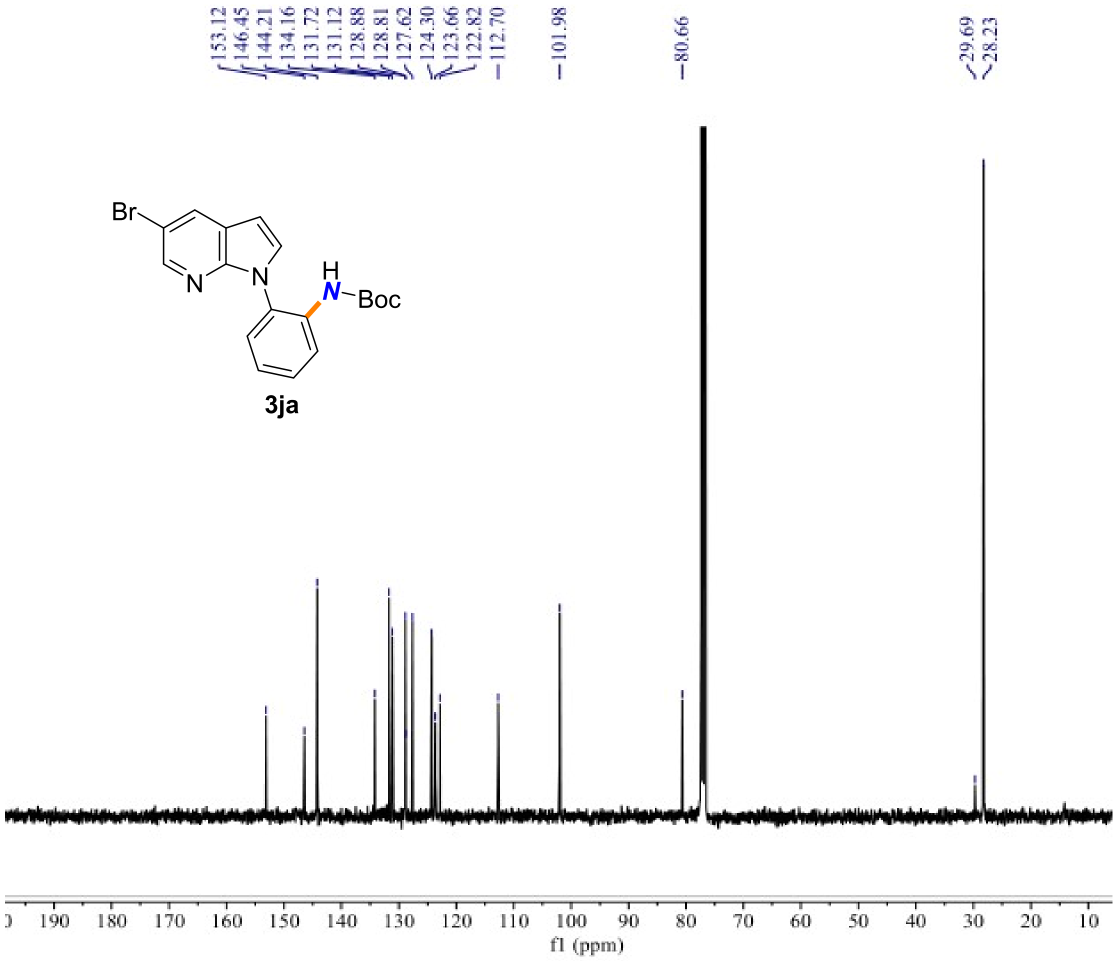
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101.98
80.66
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Boc
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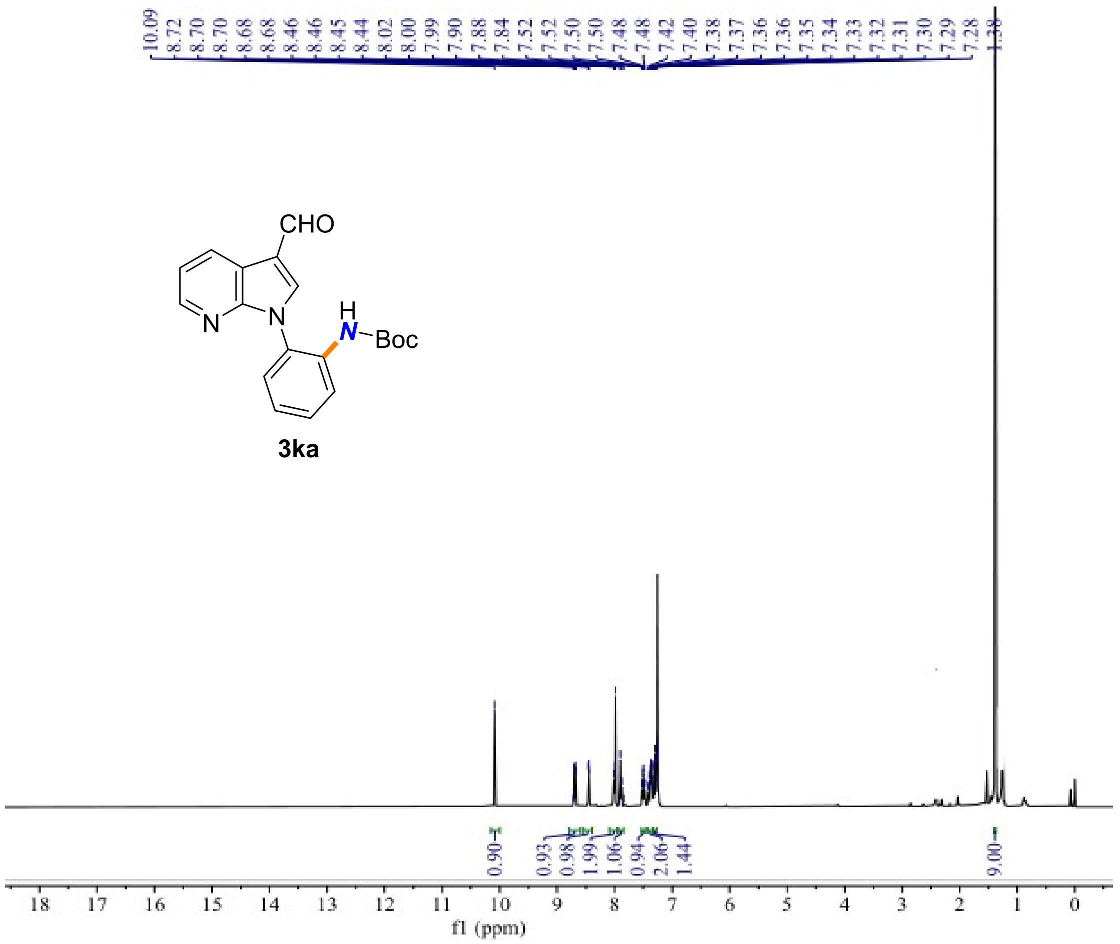
f1 (ppm)

3ja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7.90
7.88
7.84
7.52
7.52
7.50
7.50
7.48
7.48
7.42
7.40
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
1.38
CHO
N
N
H
N
Boc
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0.93
0.98
1.99
1.06
0.94
2.06
1.44
9.00
18
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9
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5
4
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1
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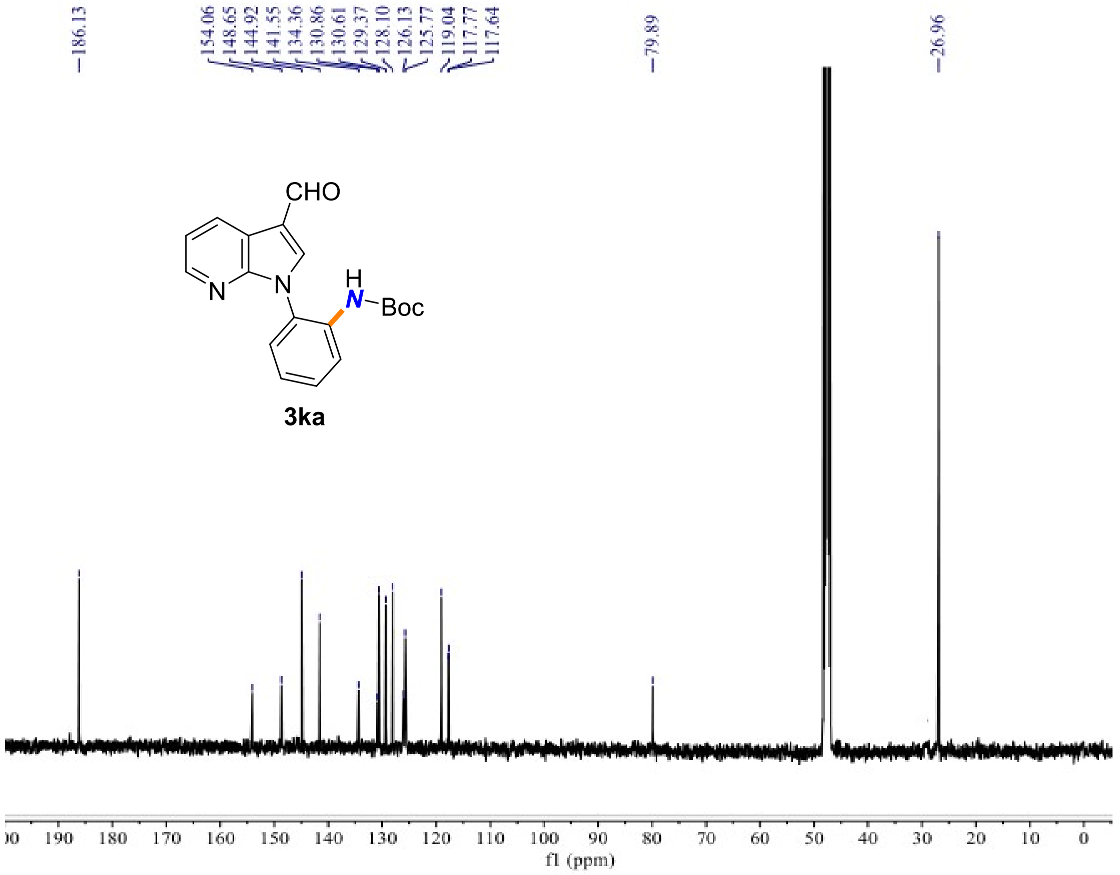
f1 (ppm)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117.77
117.64
79.89
26.96
CHO
N
N
H
N
Boc
3ka
00
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180
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90
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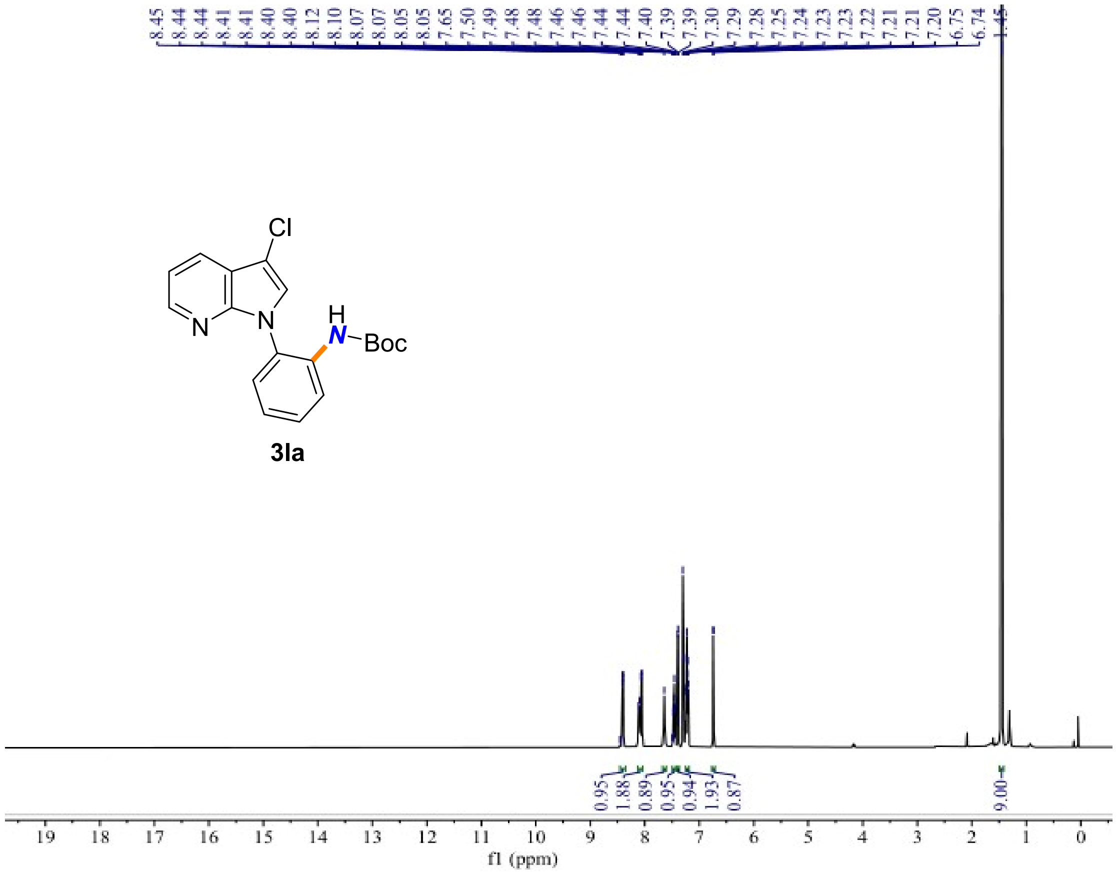
f1 (ppm)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8.07
8.05
8.05
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7.46
7.44
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7.40
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7.30
7.29
7.28
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
6.75
6.74
1.45
Cl
N
N
H
N
Boc
3la
0.95
1.88
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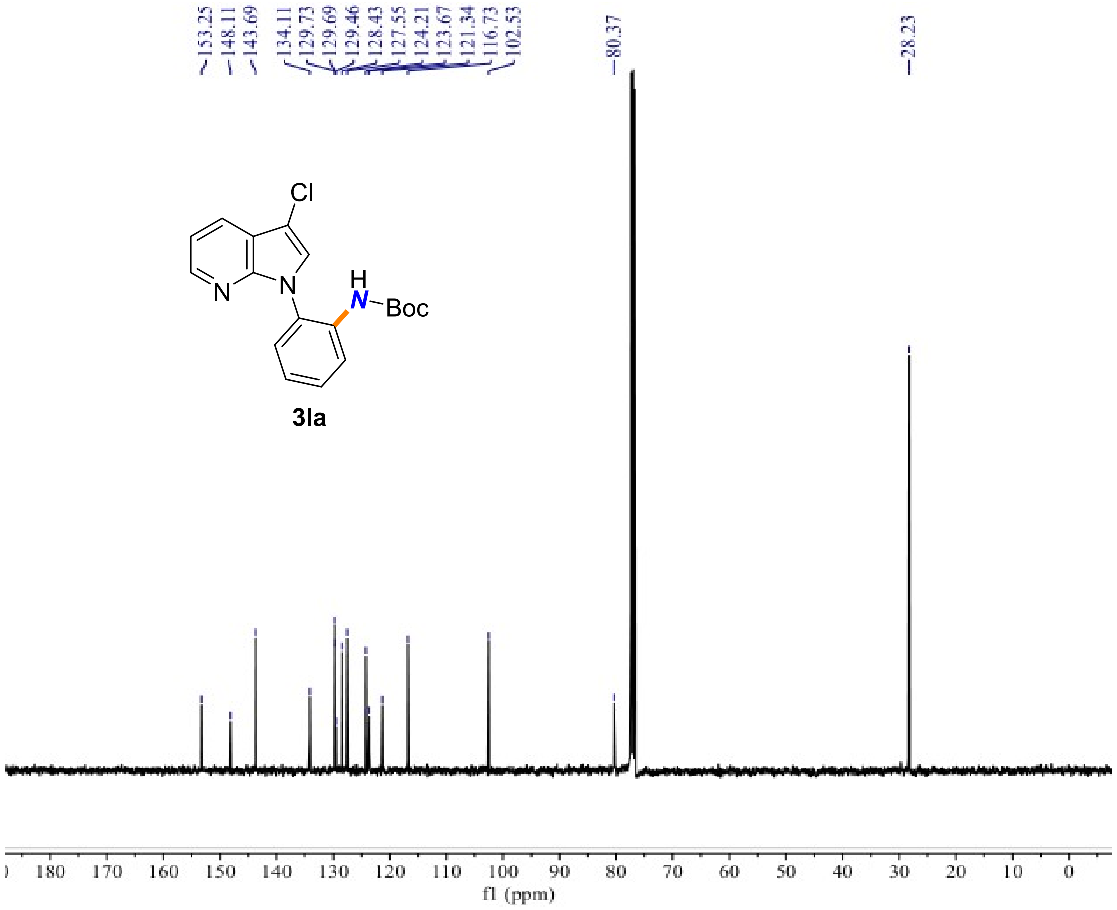
0.94
1.93
0.87
9.00
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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128.43
127.55
124.21
123.67
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116.73
102.53
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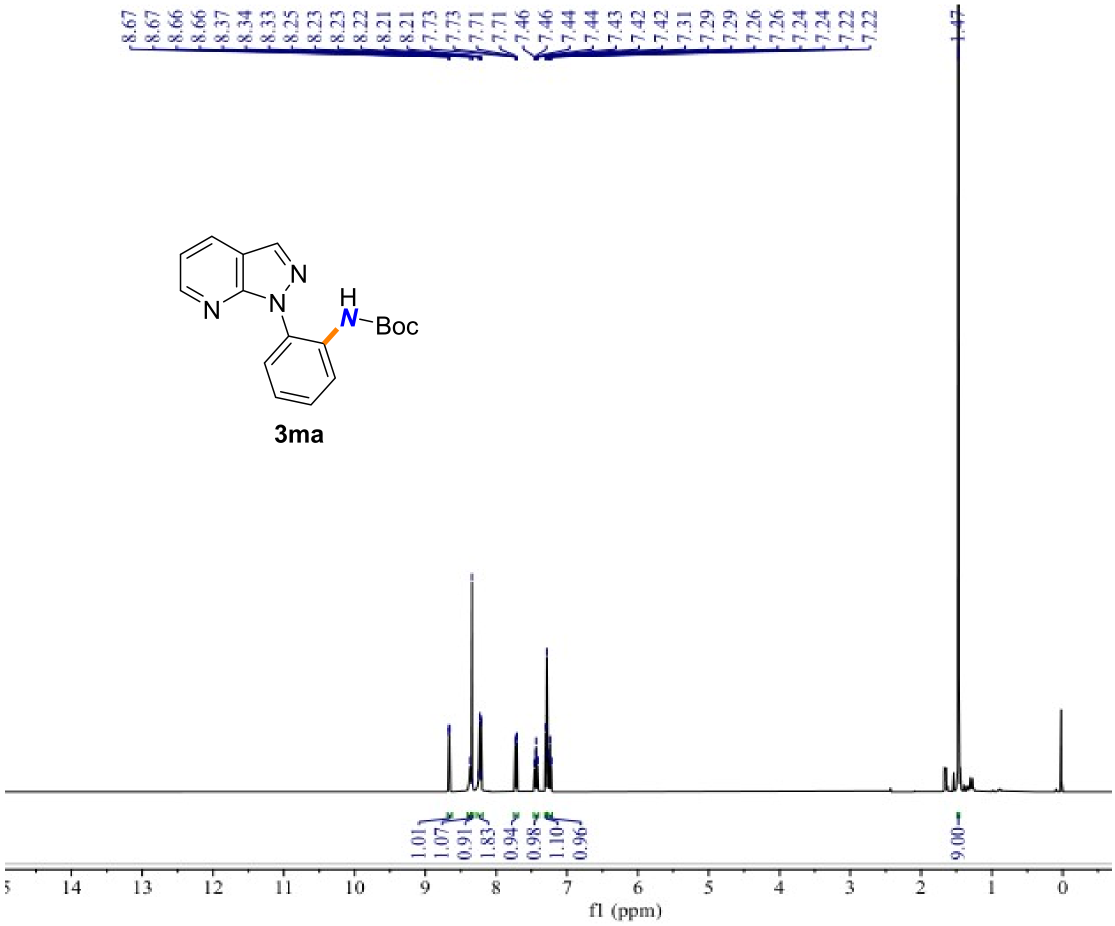
28.23
Cl
N
N
H
N
Boc
3la
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.21
8.21
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7.73
7.71
7.71
7.46
7.46
7.44
7.44
7.43
7.42
7.42
7.31
7.29
7.29
7.26
7.26
7.24
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7.22
7.22
1.47
N
N
N
H
N
Boc
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1.07
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0.94
0.98
1.10
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7
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5
4
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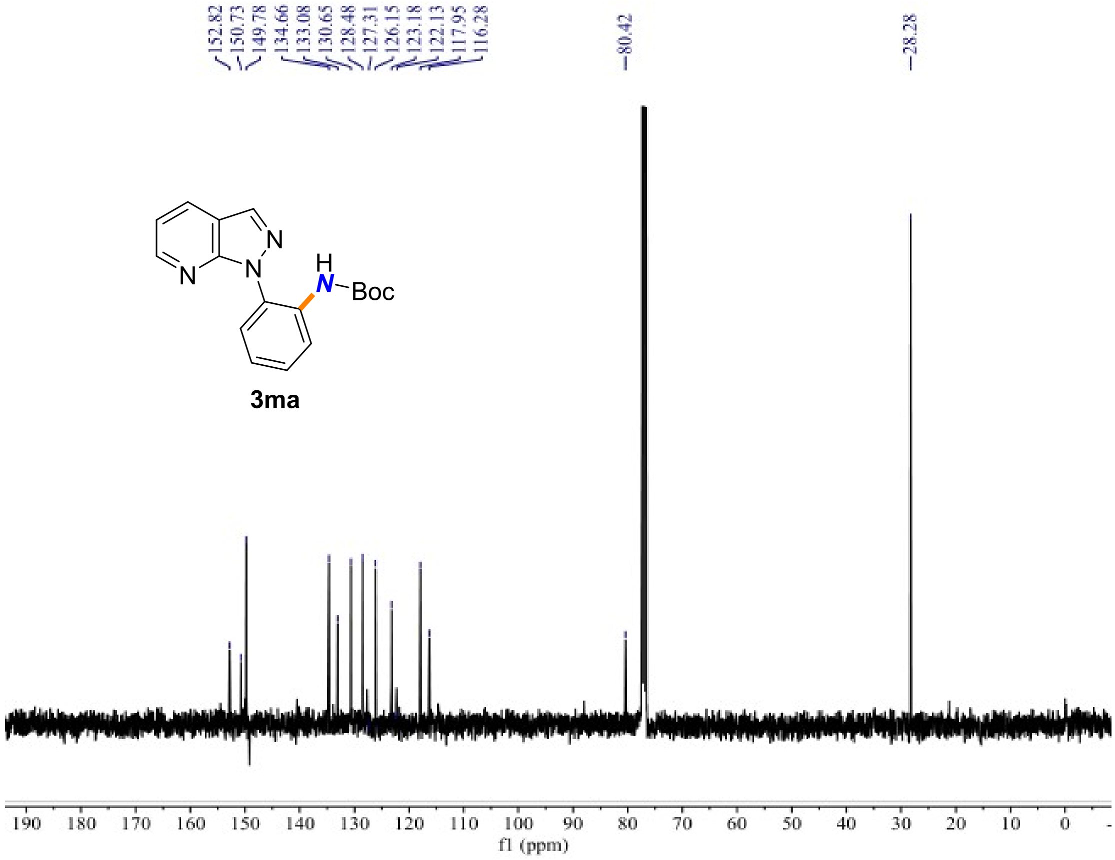
f1 (ppm)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126.15
123.18
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117.95
116.28
80.42
28.28
N
N
N
H
N
Boc
190
180
170
160
150
140
130
120
110
100
90
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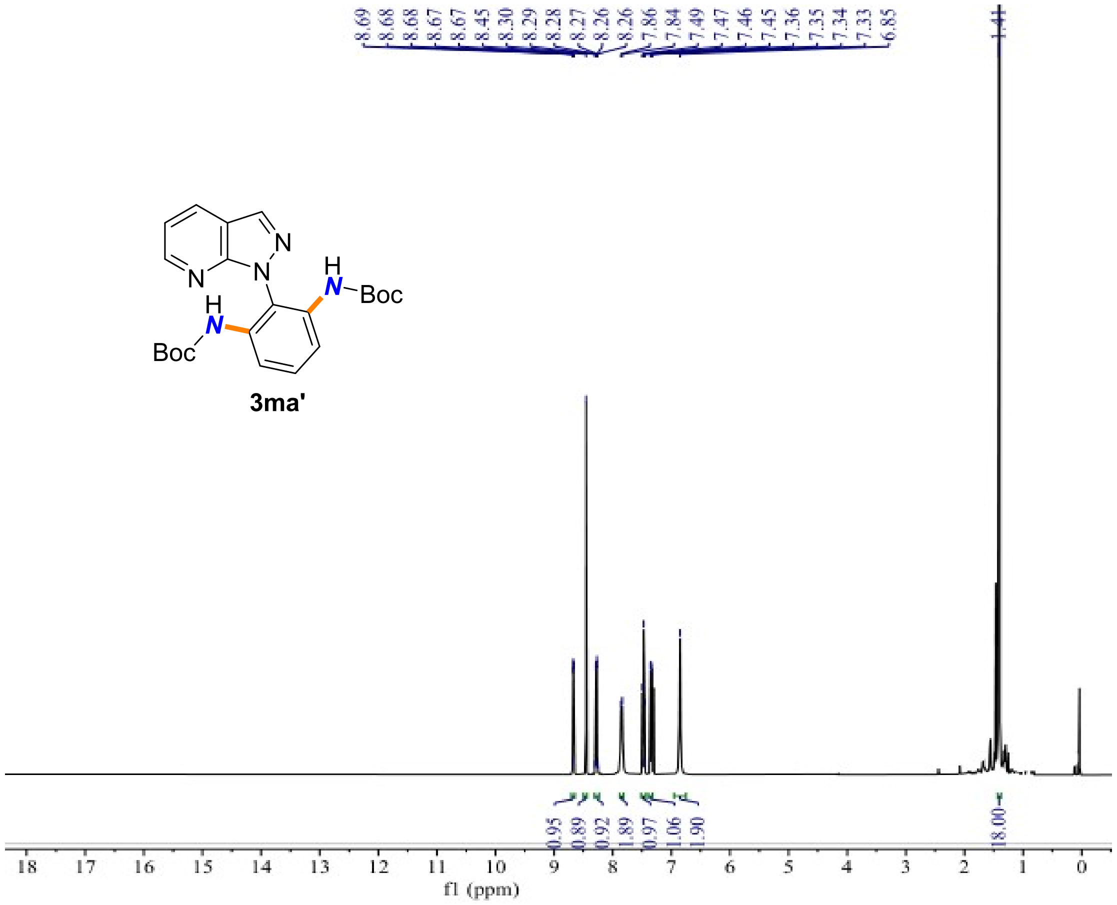
50
40
30
20
10
0
f1 (ppm)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8.26
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7.84
7.49
7.47
7.46
7.45
7.36
7.35
7.34
7.33
6.85
1.41
N
N
N
H
N
Boc
H
N
Boc
3ma'
0.95
0.89
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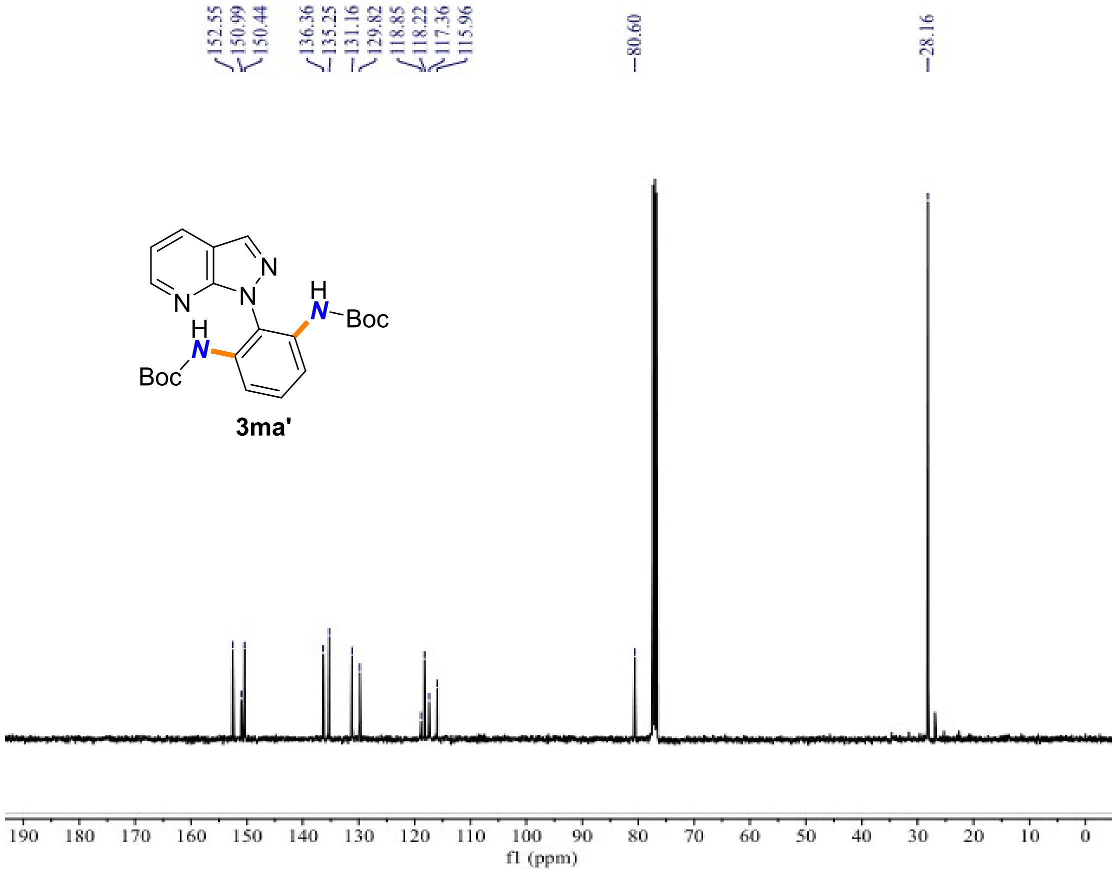
0.97
1.06
1.90
18.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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28.16
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Boc
H
N
Boc
3ma'
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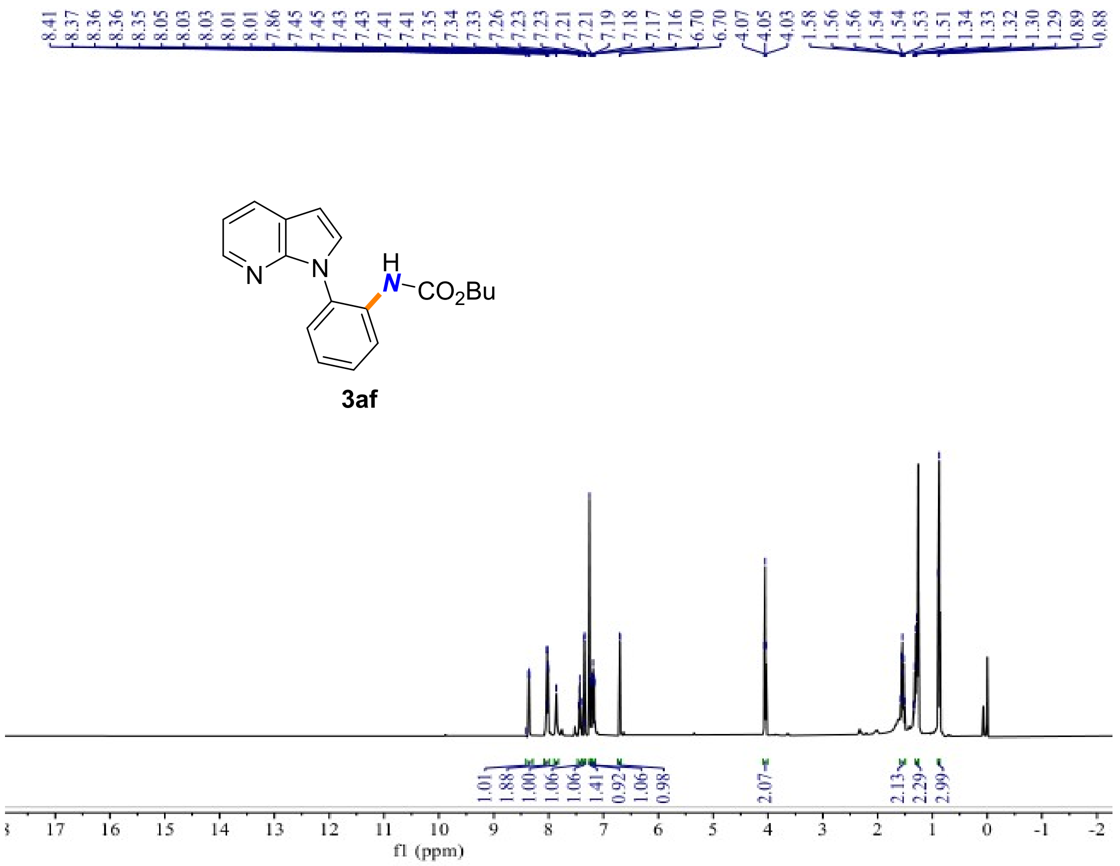
f1 (ppm)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7.26
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7.23
7.21
7.21
7.19
7.18
7.17
7.16
6.70
4.07
4.05
4.03
1.58
1.56
1.56
1.54
1.54
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1.51
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1.33
1.32
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1.29
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0.88
N
N
H
N
CO2Bu
3af
1.01
1.88
1.00
1.06
1.06
1.41
0.92
1.06
0.98
2.07
2.13
2.29
2.99
17
16
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9
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6
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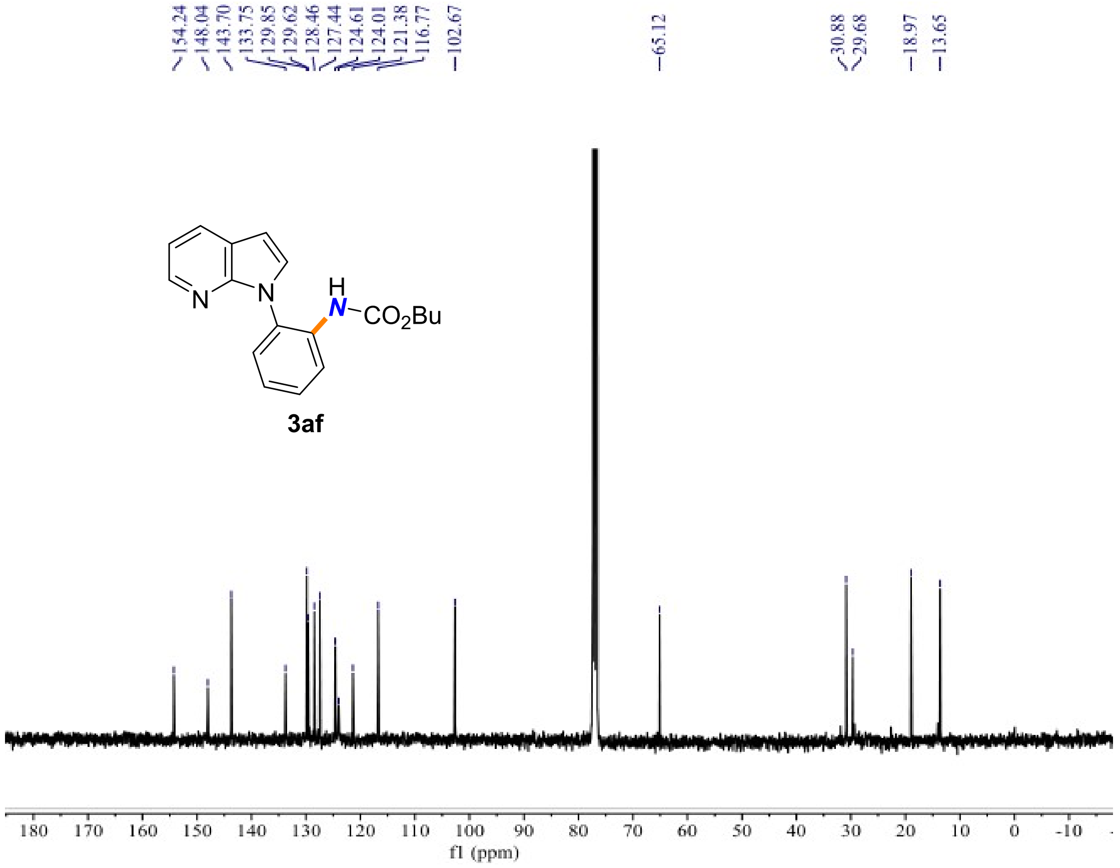
-2
f1 (ppm)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29.68
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13.65
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N
H
N
CO2Bu
3af
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100
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80
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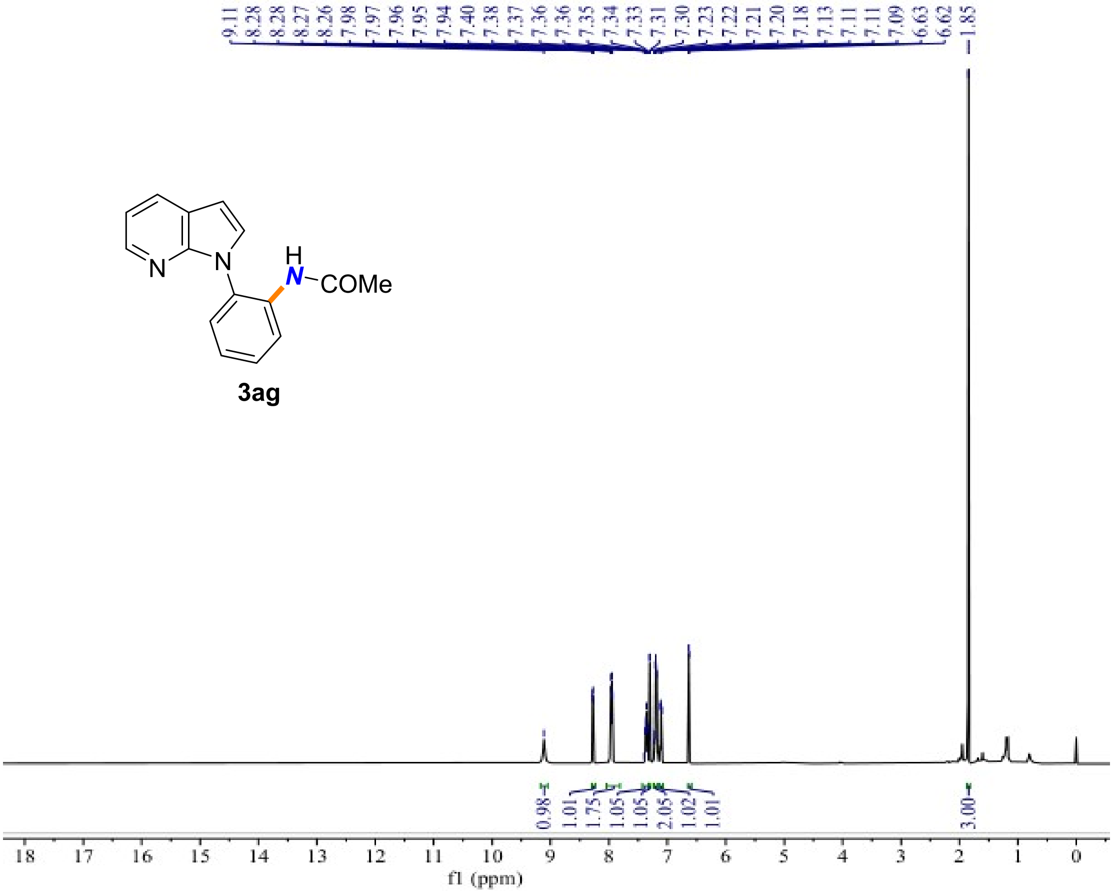
f1 (ppm)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7.23
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7.21
7.20
7.18
7.13
7.11
7.11
7.09
6.63
6.62
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N
H
N
COMe
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1.75
1.05
1.05
2.05
1.02
1.01
3.00
18
17
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3
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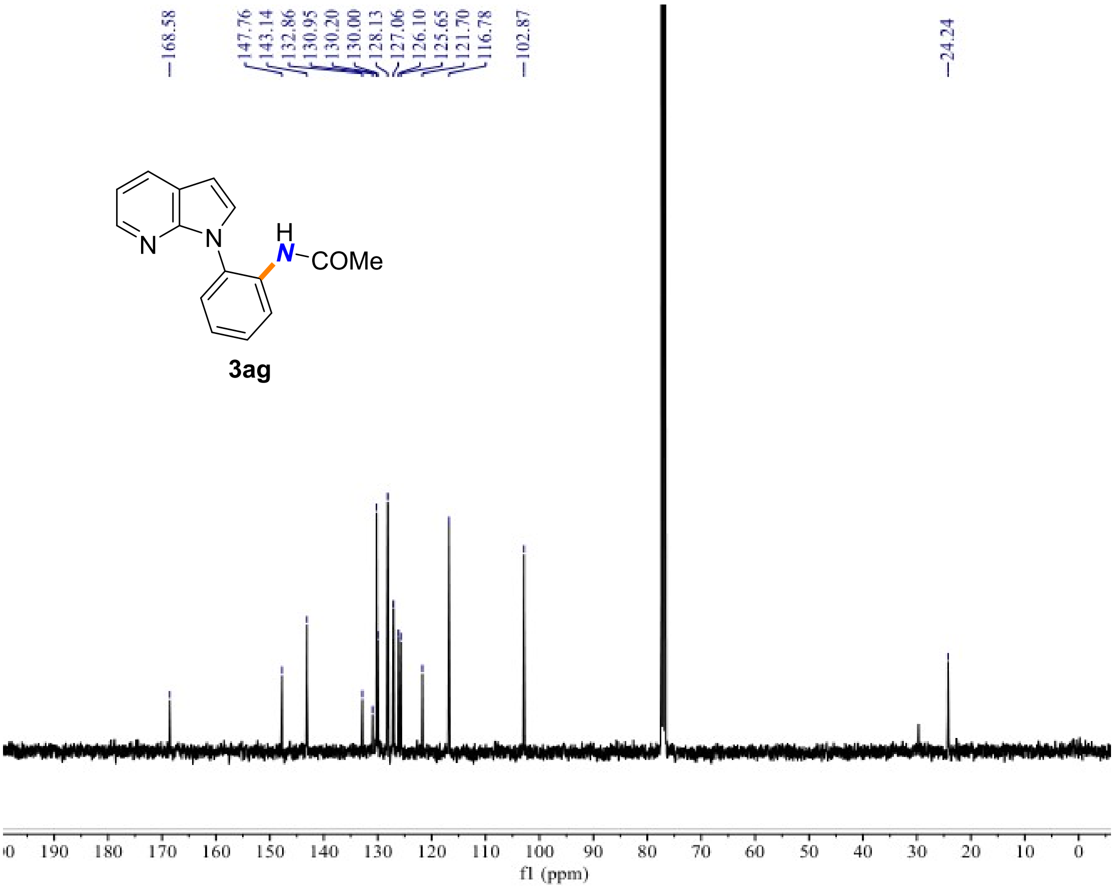
f1 (ppm)

3ag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102.87
24.24
N
N
H
N
COMe
0
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180
170
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100
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80
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30
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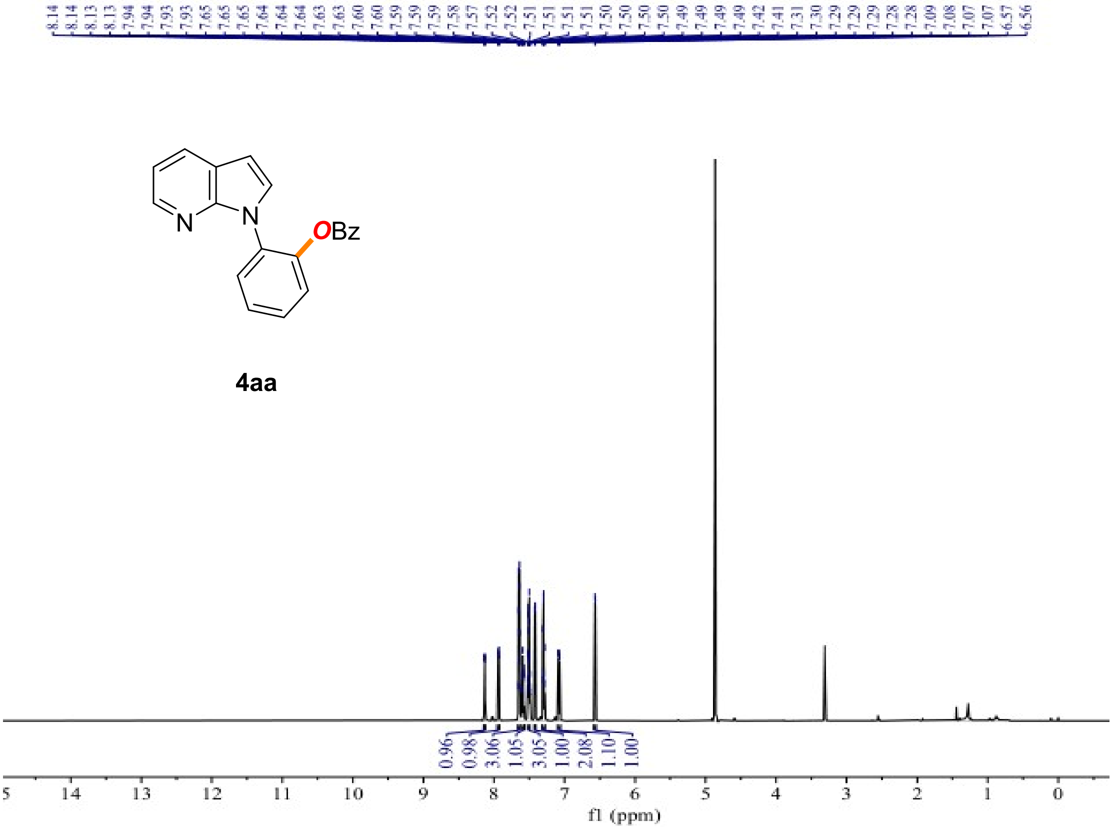
f1 (ppm)

3ag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7.08
7.07
7.07
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6.56
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0.98
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3.05
1.00
2.08
1.10
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11
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4
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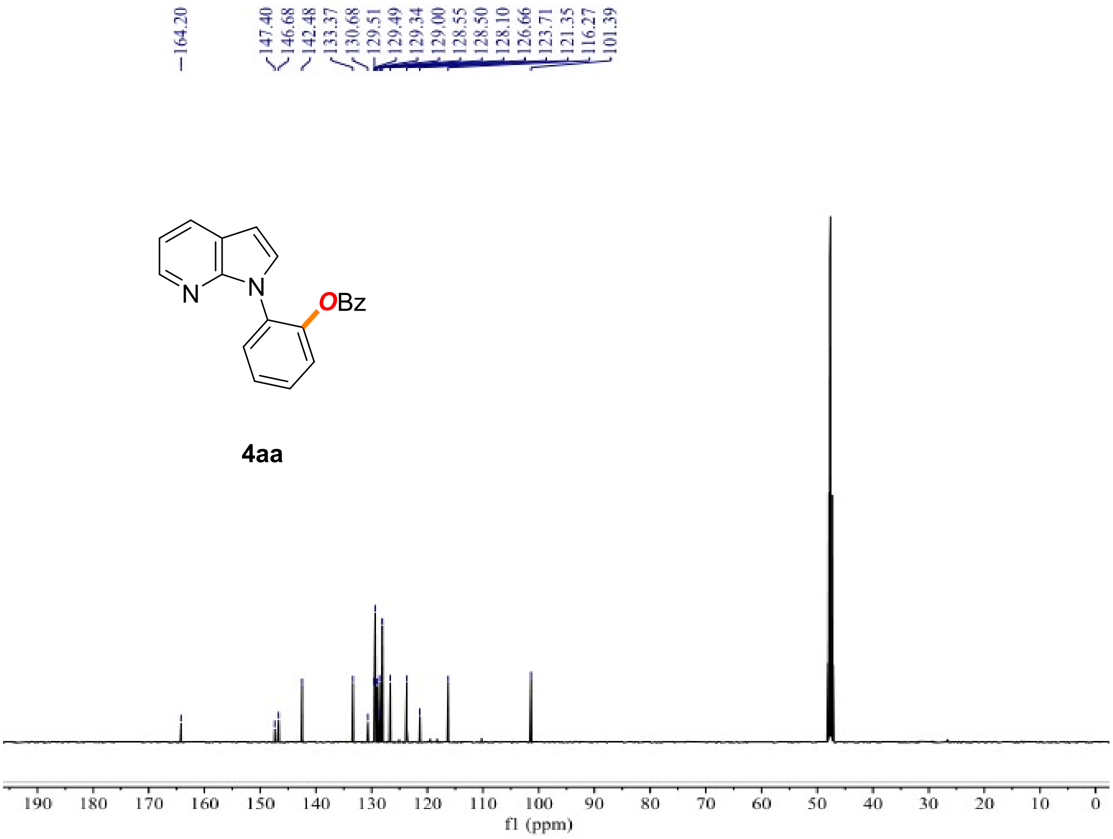
f1 (ppm)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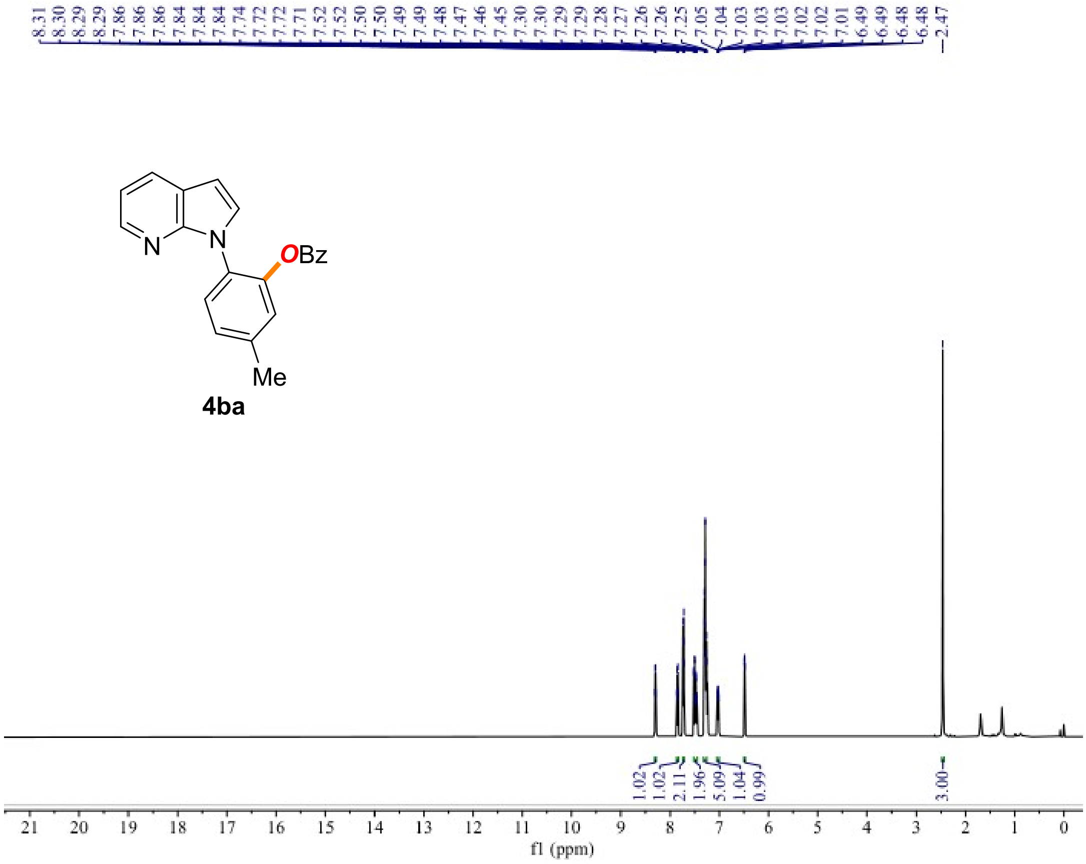
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7.04
7.03
7.03
7.03
7.02
7.02
7.01
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6.48
6.48
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1.02
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1.04
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3.00
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5
4
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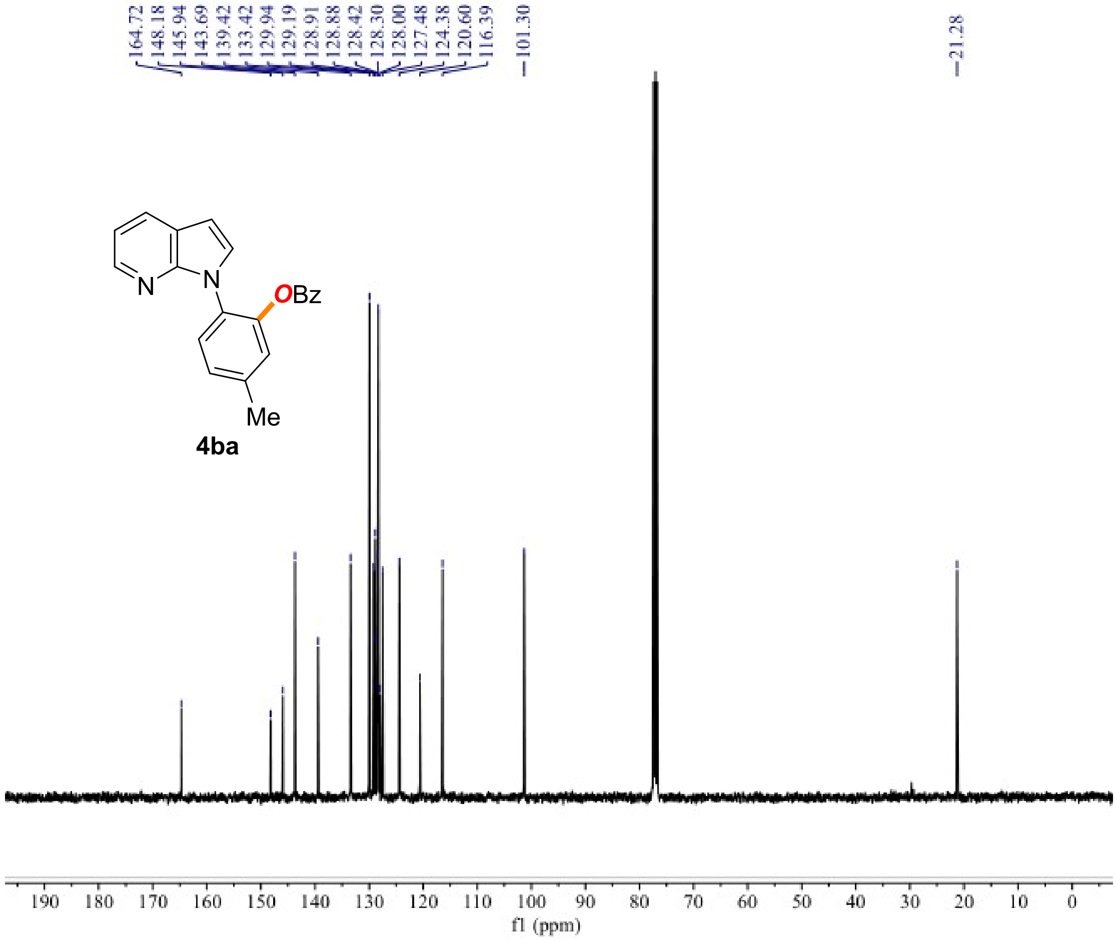
f1 (ppm)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21.28
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OBz
Me
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180
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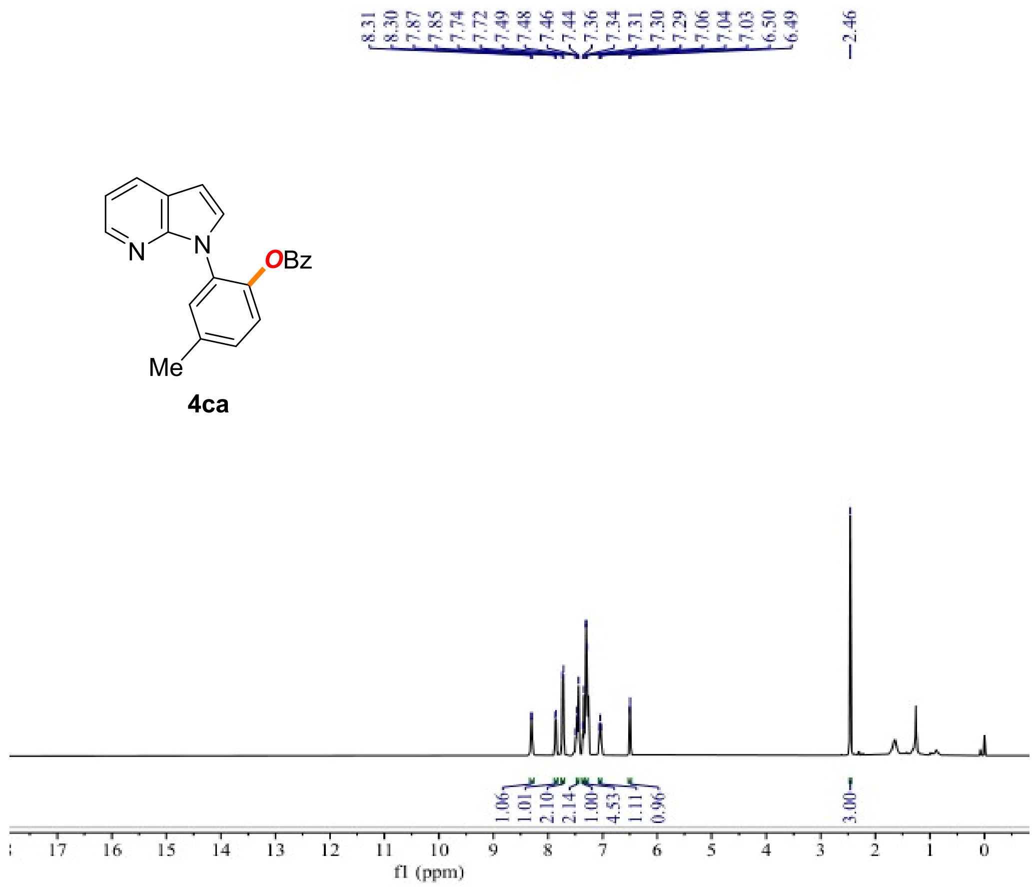
f1 (ppm)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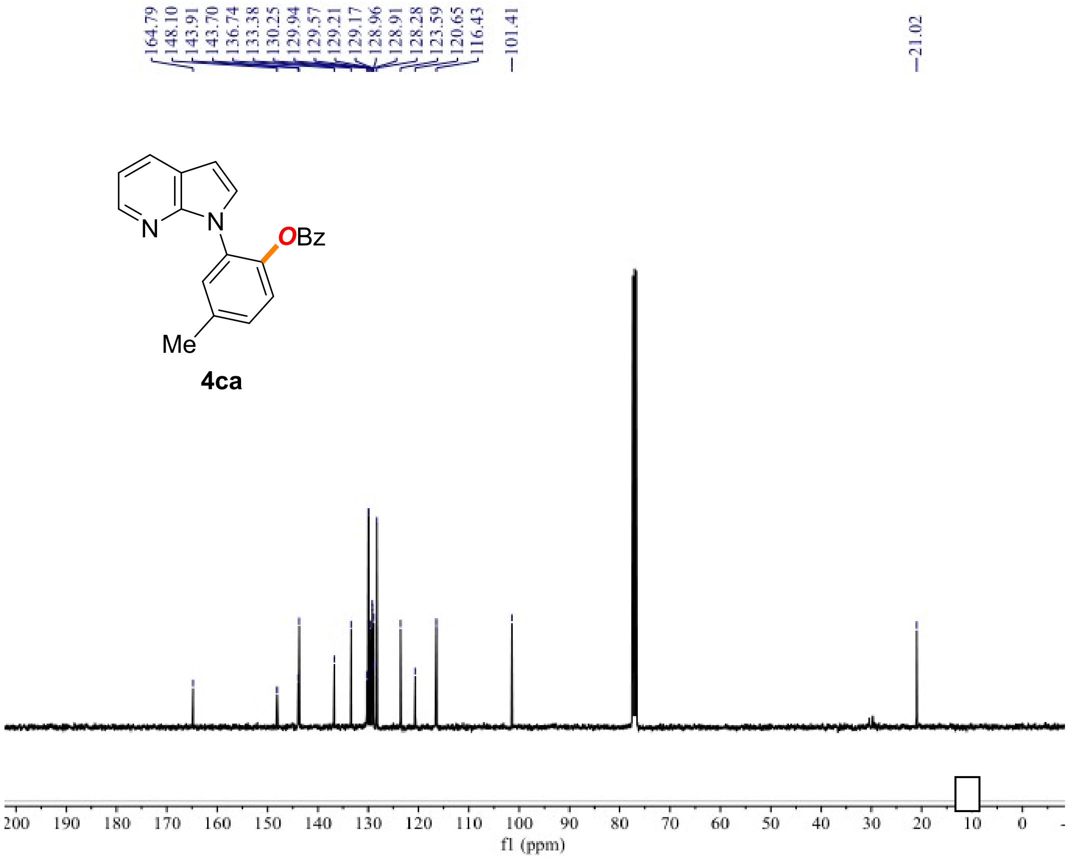
f1 (ppm)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120.65
116.43
101.41
21.02
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N
OBz
Me
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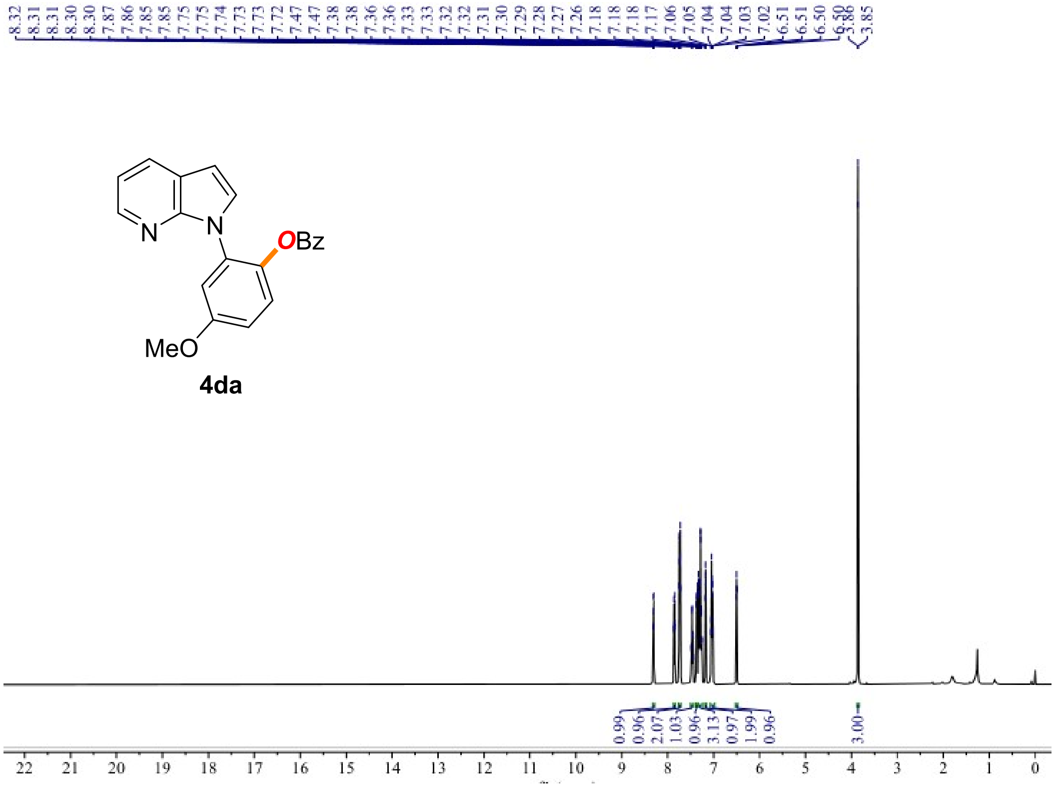
f1 (ppm)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7.18
7.17
7.06
7.05
7.04
7.04
7.03
7.02
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6.51
6.50
6.50
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OBz
MeO
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1.03
0.96
3.13
0.97
1.99
0.96
3.00
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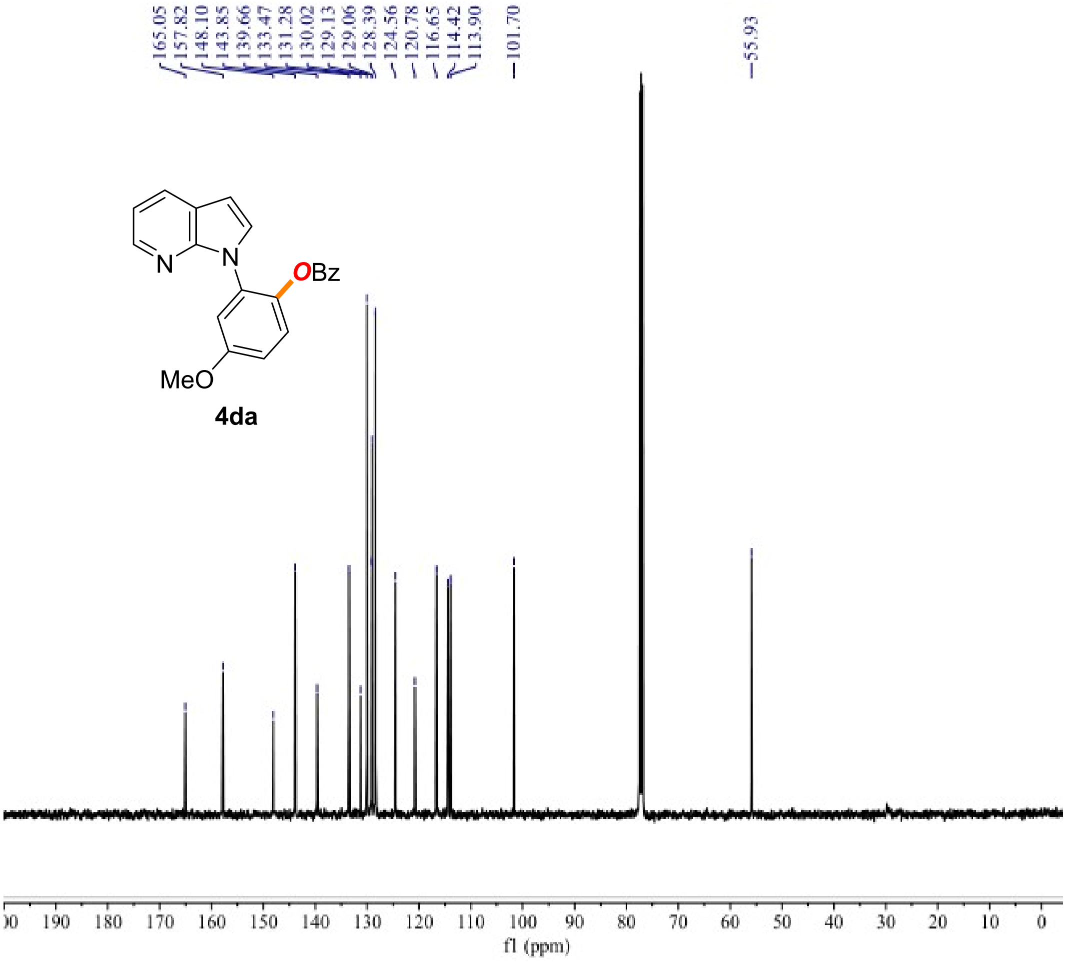
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128.39
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120.78
116.65
114.42
113.90
101.70
55.93
N
N
OBz
MeO
4da
190
180
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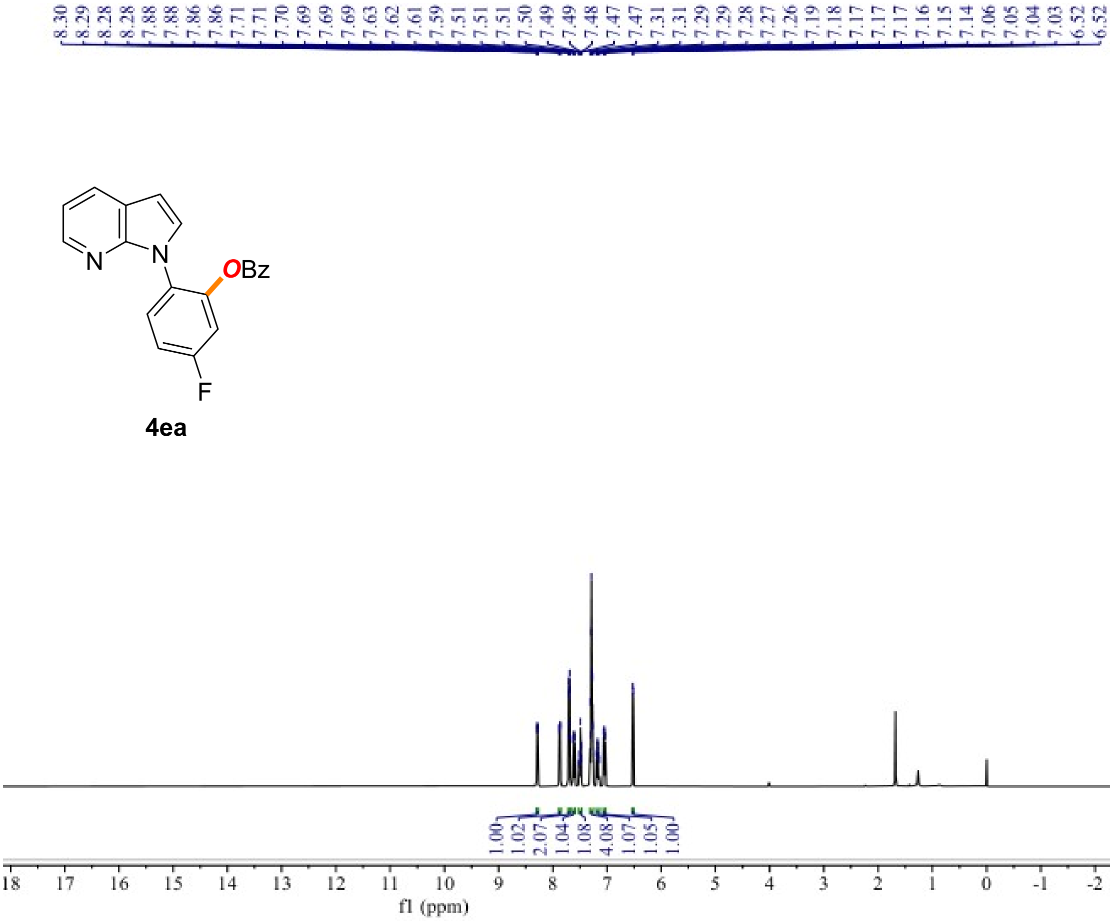
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7.51
7.51
7.50
7.49
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7.47
7.47
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7.31
7.29
7.29
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7.27
7.26
7.19
7.18
7.17
7.17
7.17
7.16
7.15
7.14
7.06
7.05
7.04
7.03
6.52
6.52
N
N
OBz
F
4ea
1.00
1.02
2.07
1.04
1.08
4.08
1.07
1.05
1.00
18
17
16
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9
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7
6
5
4
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2
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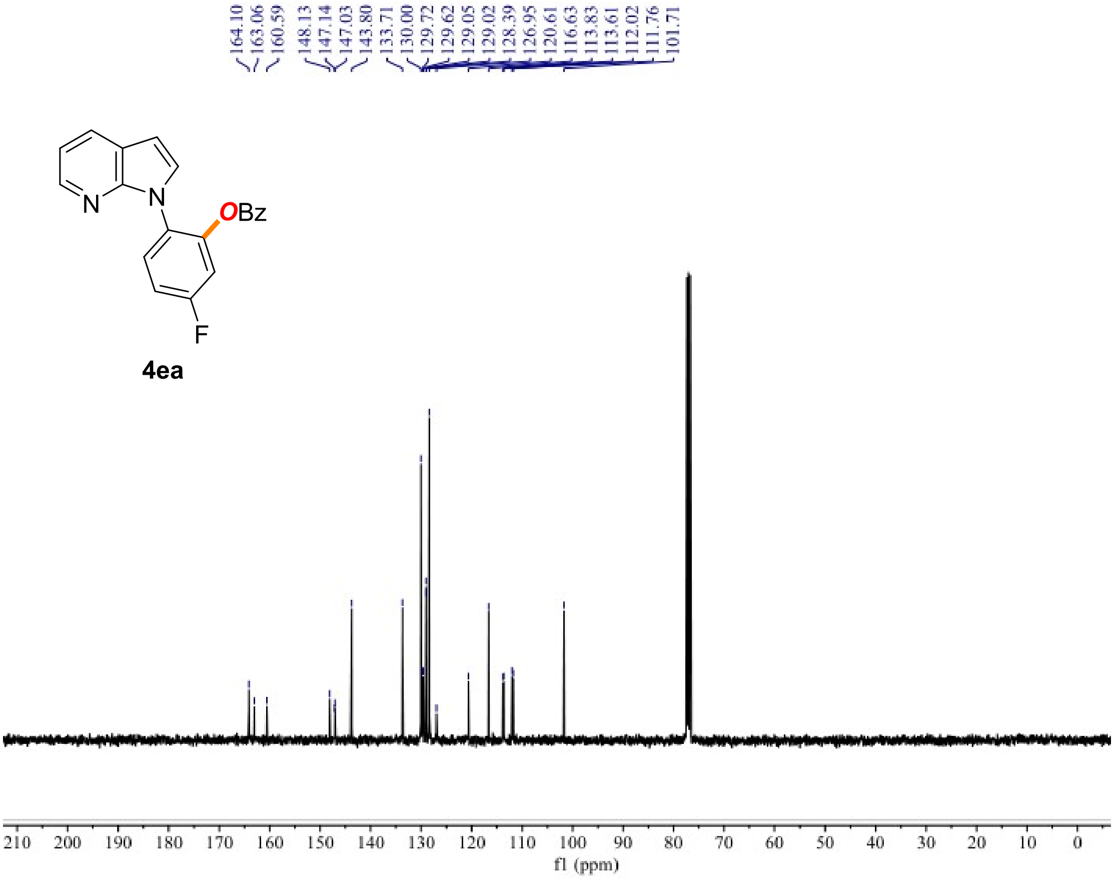
0
-1
-2
f1 (ppm)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129.02
128.39
126.95
120.61
116.63
113.83
113.61
112.02
111.76
101.71
N
N
OBz
F
4ea
210
200
190
180
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110
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40
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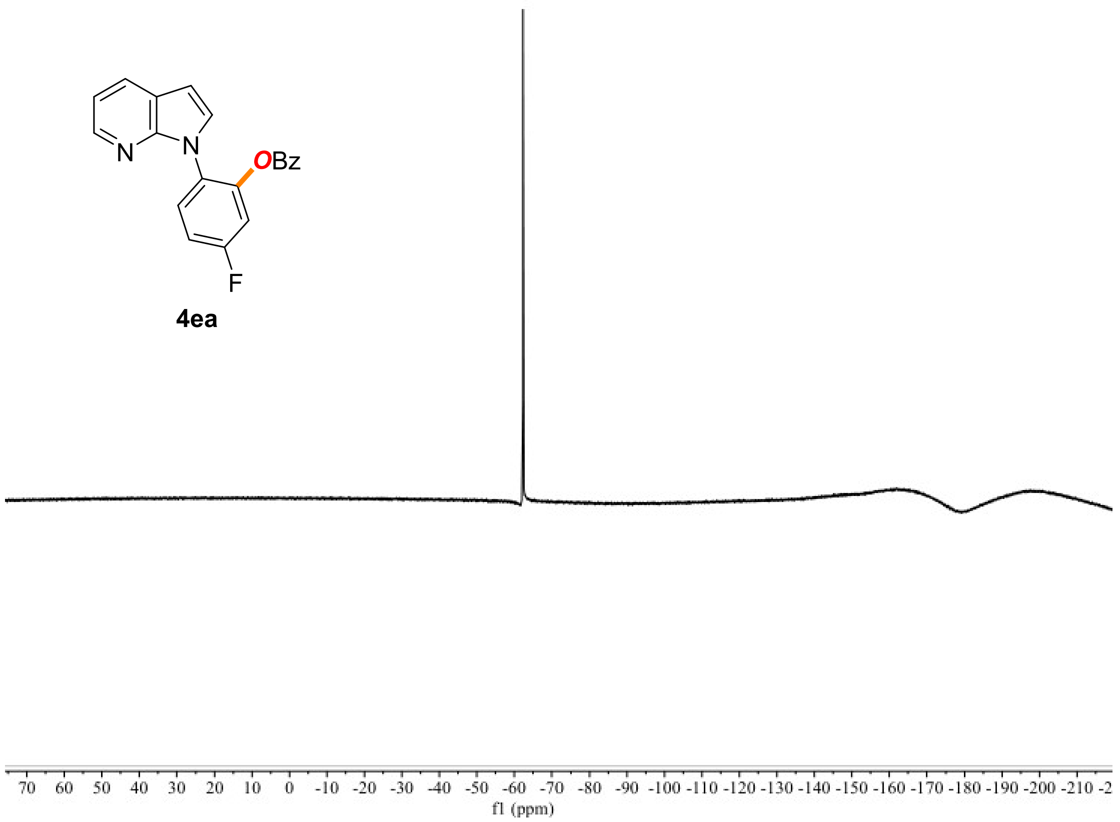
f1 (ppm)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OBz
F
4ea
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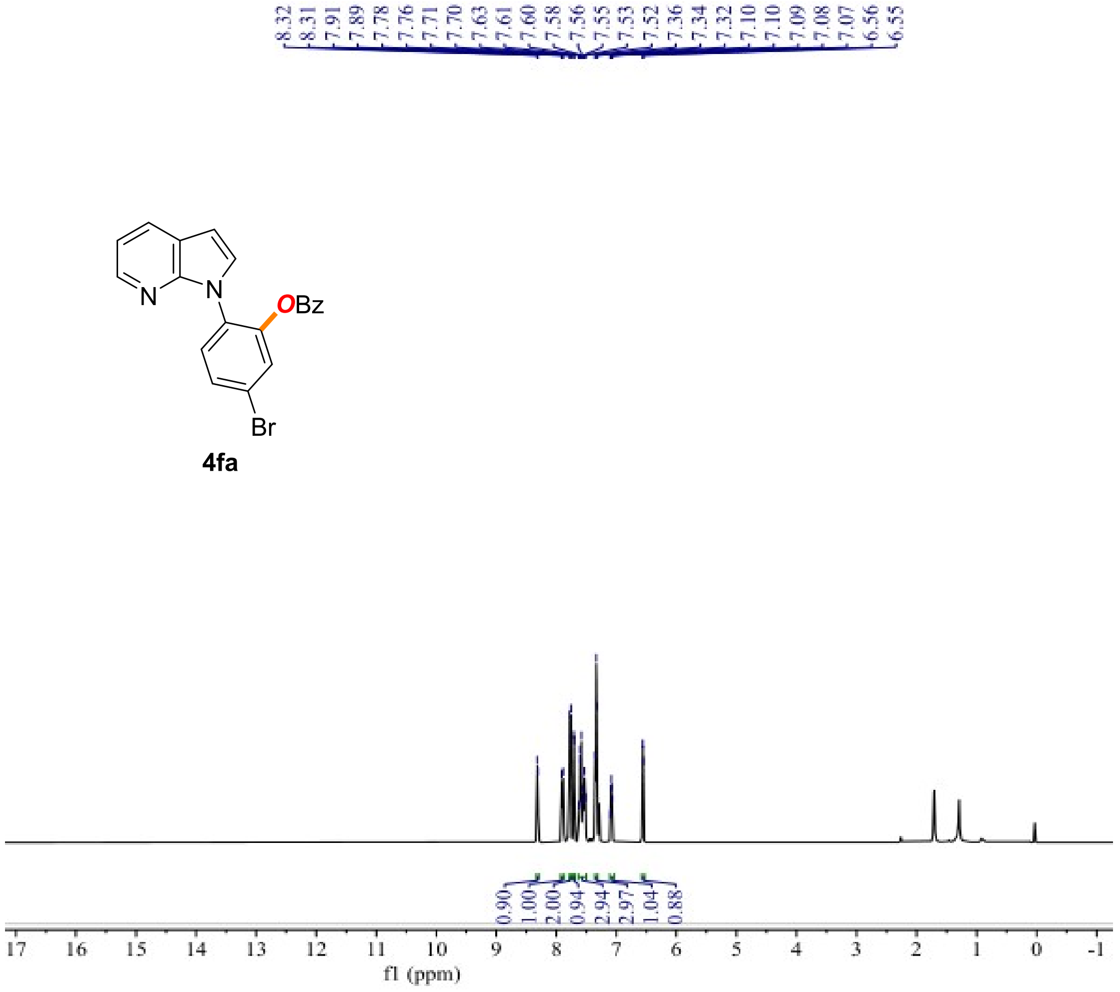
f1 (ppm)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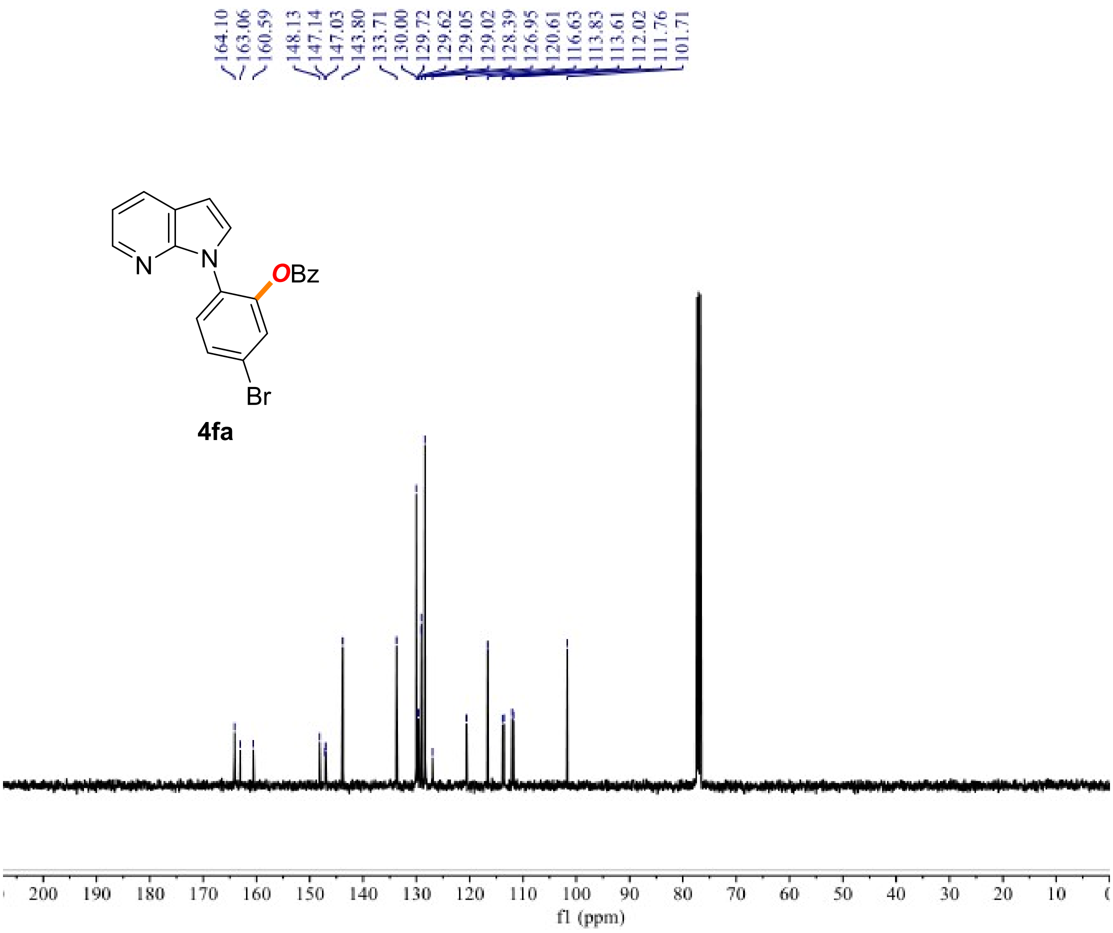
7.60
7.58
7.56
7.55
7.53
7.52
7.36
7.34
7.32
7.10
7.10
7.09
7.08
7.07
6.56
6.55
N
N
OBz
Br
4fa
0.90
1.00
2.00
0.94
2.94
2.97
1.04
0.88
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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129.02
128.39
126.95
120.61
116.63
113.83
113.61
112.02
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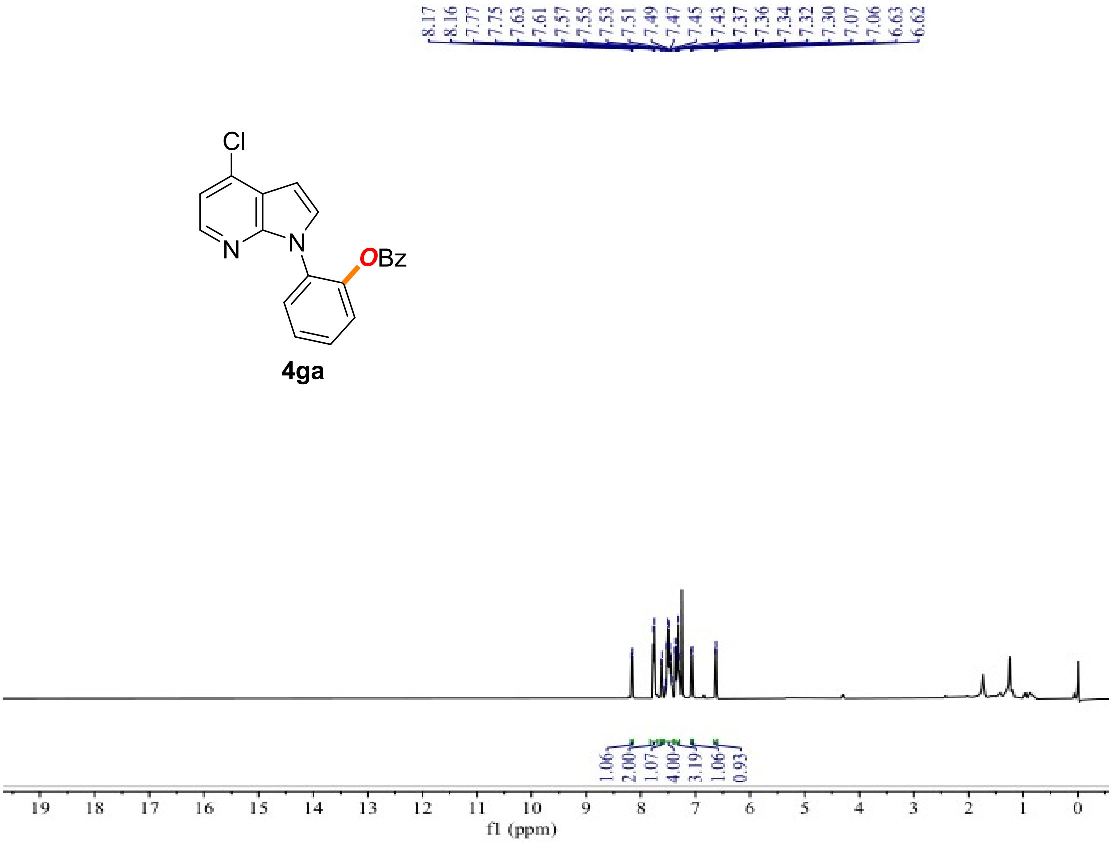
N
N
OBz
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

4fa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7.55
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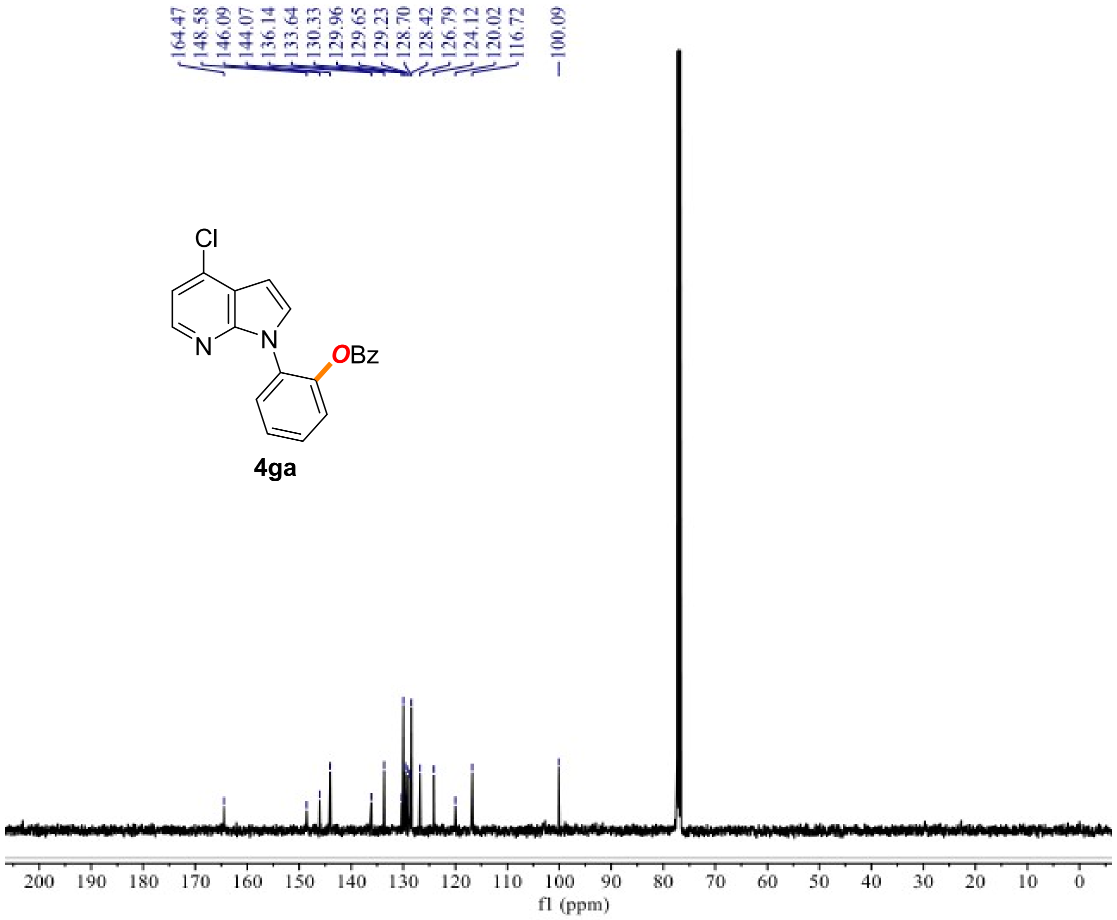
7.51
7.49
7.47
7.45
7.43
7.37
7.36
7.34
7.32
7.30
7.07
7.06
6.63
6.62
Cl
N
N
OBz
1.06
2.00
1.07
4.00
3.19
1.06
0.93
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

4ga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130.33
129.96
129.65
129.23
128.70
128.42
126.79
124.12
120.02
116.72
100.09
Cl
N
N
OBz
200
190
180
170
160
150
140
130
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110
100
90
80
70
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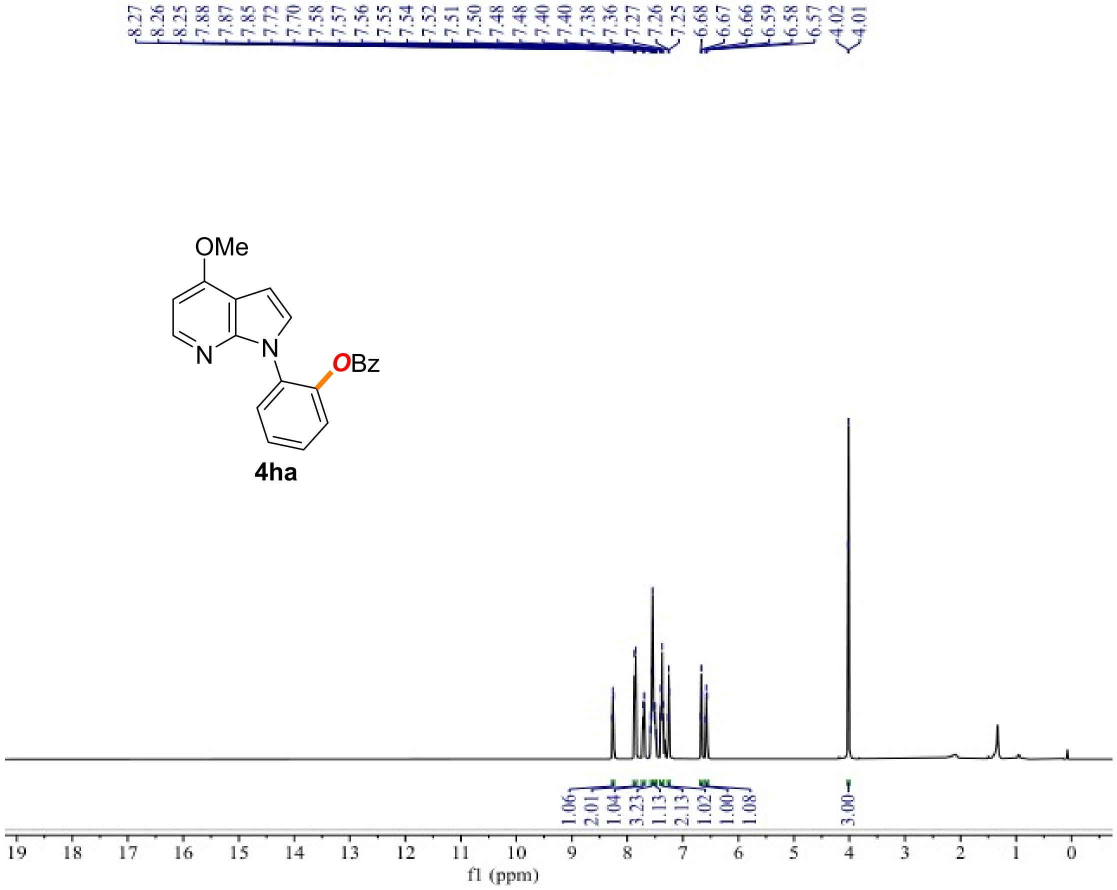
50
40
30
20
10
0
f1 (ppm)

4ga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7.54
7.52
7.51
7.50
7.48
7.40
7.40
7.38
7.36
7.27
7.26
7.25
6.68
6.67
6.66
6.59
6.58
6.57
4.02
4.01
OMe
N
N
OBz
1.06
2.01
1.04
3.23
1.13
2.13
1.02
1.00
1.08
3.00
19
18
17
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11
10
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7
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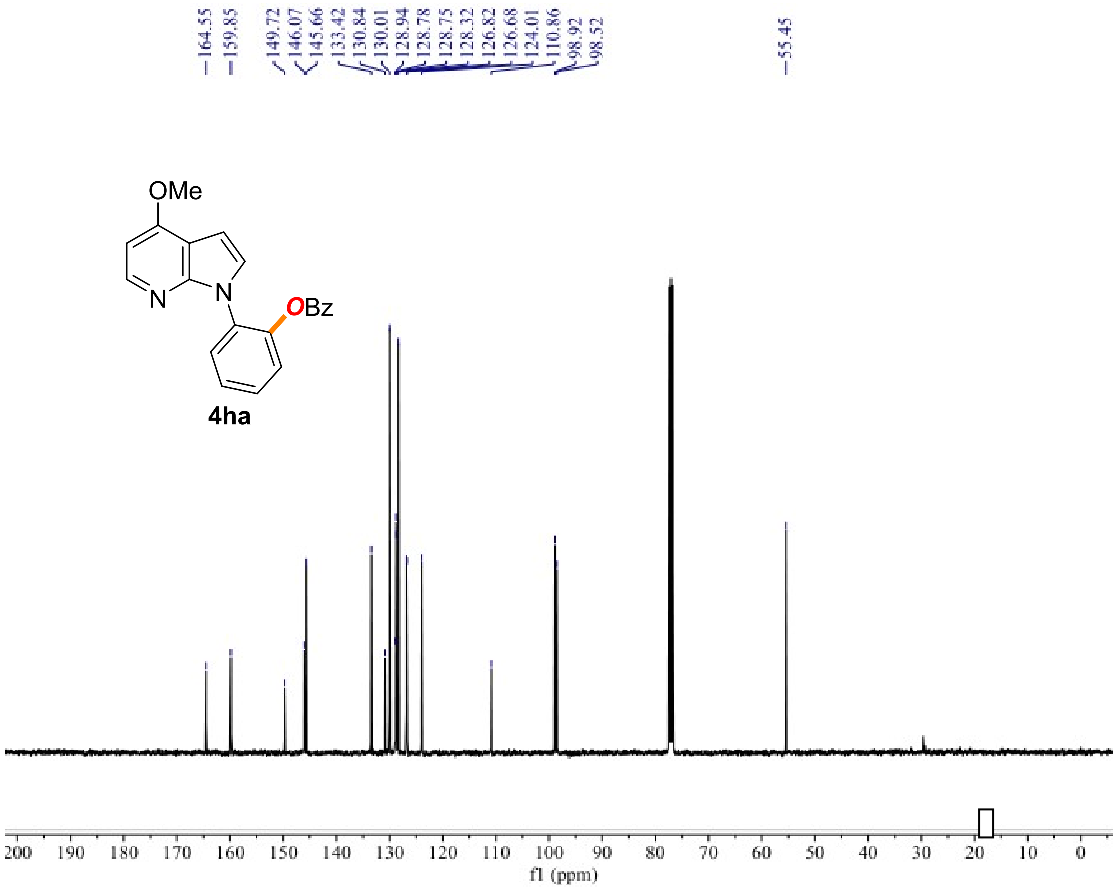
5
4
3
2
1
0
f1 (ppm)

4ha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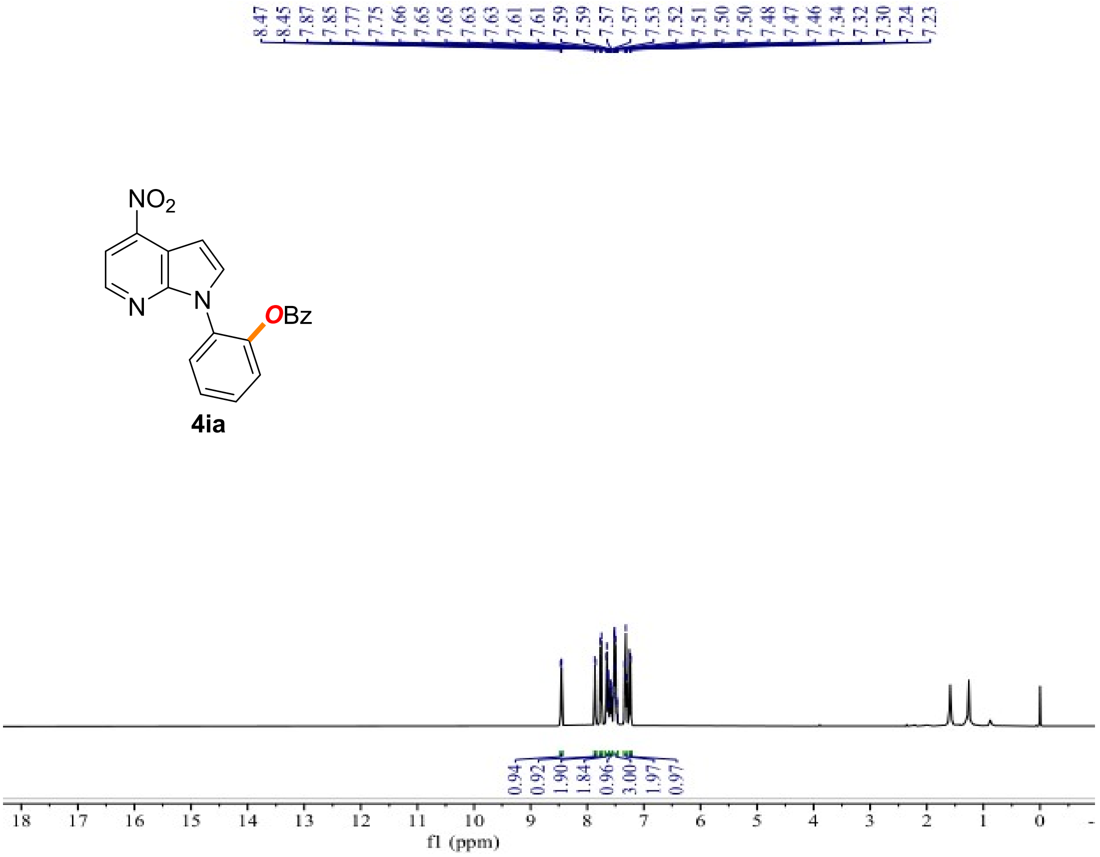
130.01
128.94
128.78
128.75
128.32
126.82
126.68
124.01
110.86
98.92
98.52
55.45
OMe
N
N
OBz
4ha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.61
7.59
7.59
7.57
7.57
7.53
7.52
7.51
7.50
7.50
7.48
7.47
7.46
7.34
7.32
7.30
7.24
7.23
NO$_2$
N
N
OBz
4ia
0.94
0.92
1.90
1.84
0.96
3.00
1.97
0.97
18
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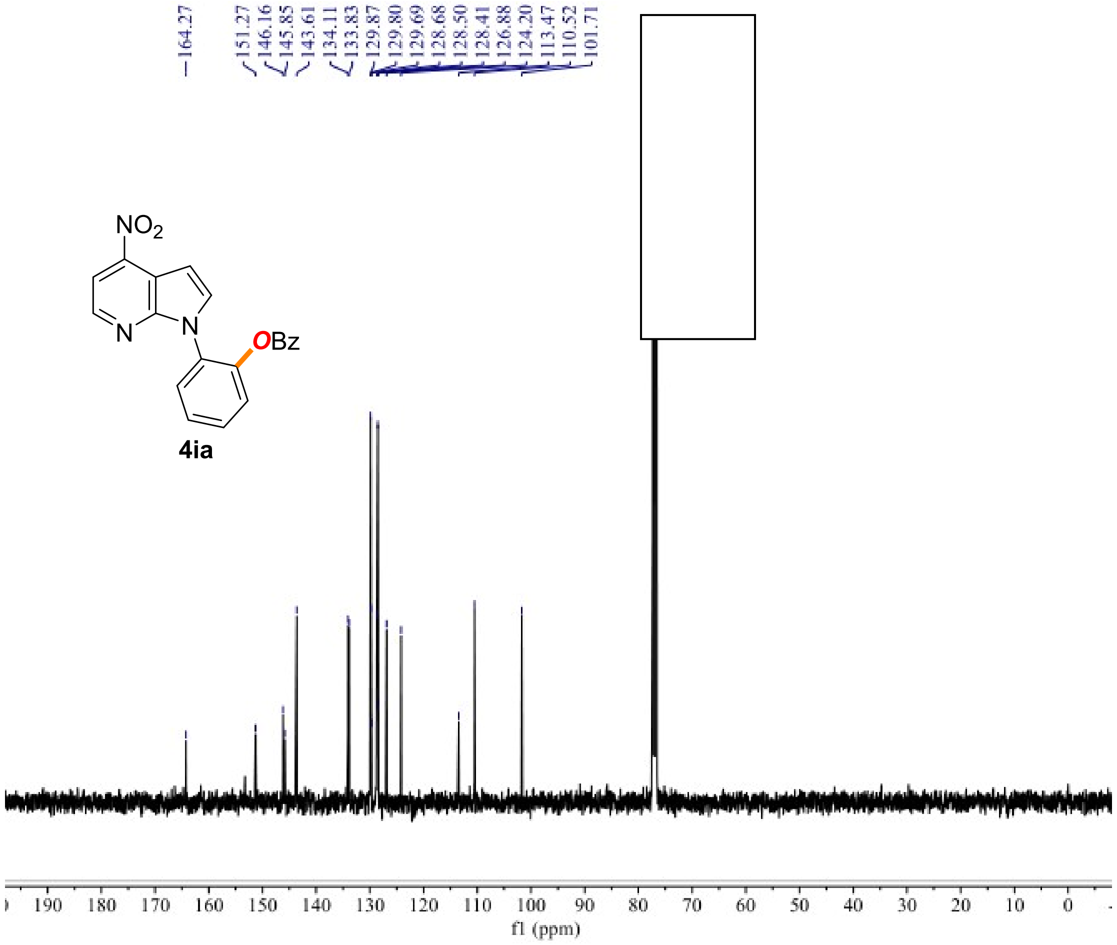
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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133.83
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129.69
128.68
128.50
128.41
126.88
124.20
113.47
110.52
101.71
NO_2
N
N
OBz
190
180
170
160
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110
100
90
80
70
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50
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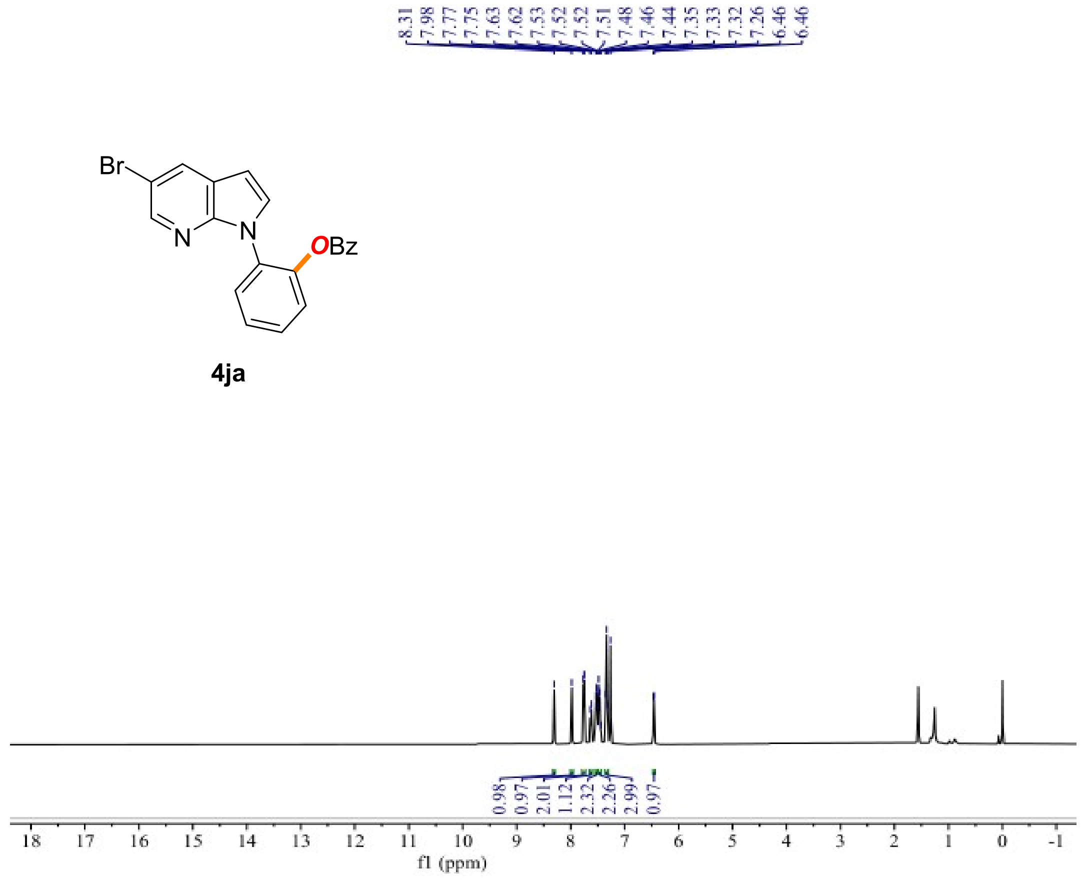
30
20
10
0
f1 (ppm)

4ia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7.51
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7.44
7.35
7.33
7.32
7.26
6.46
6.46
Br
N
N
OBz
0.98
0.97
2.01
1.12
2.32
2.26
2.99
0.97
18
17
16
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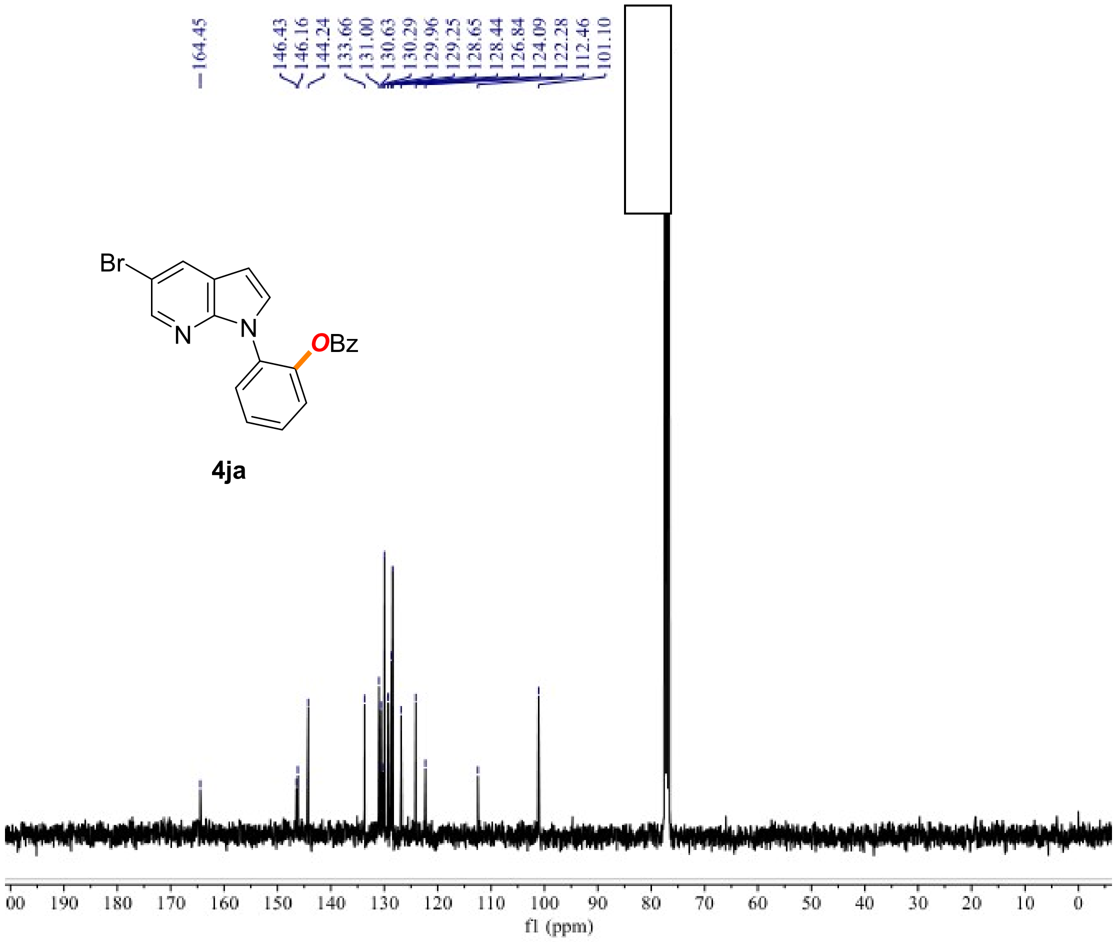
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

4ja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130.29
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129.25
128.65
128.44
126.84
124.09
122.28
112.46
101.10
Br
N
N
OBz
00
190
180
170
160
150
140
130
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110
100
90
80
70
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50
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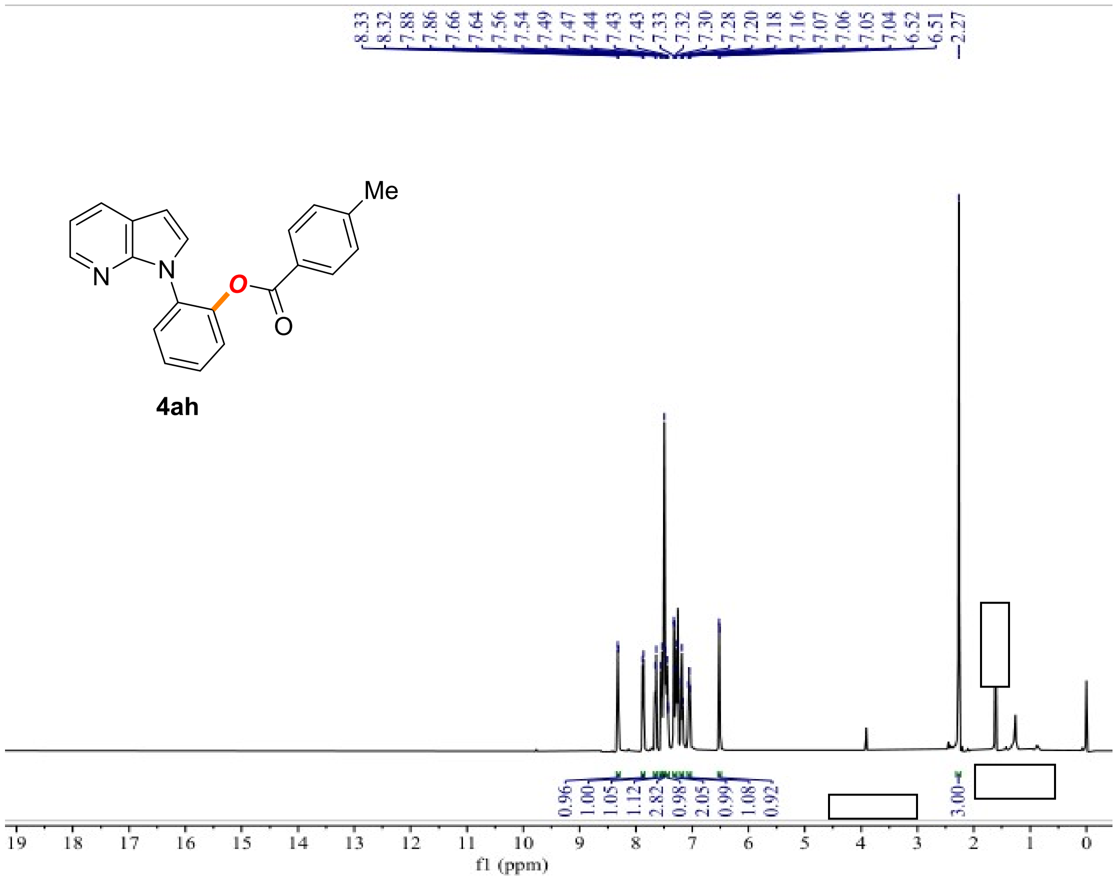
30
20
10
0
f1 (ppm)

4ja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7.47
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7.43
7.33
7.32
7.30
7.28
7.20
7.18
7.16
7.07
7.06
7.05
7.04
6.52
6.51
2.27
Me
N
N
O
O
0.96
1.00
1.05
1.12
2.82
0.98
2.05
0.99
1.08
0.92
3.00
19
18
17
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14
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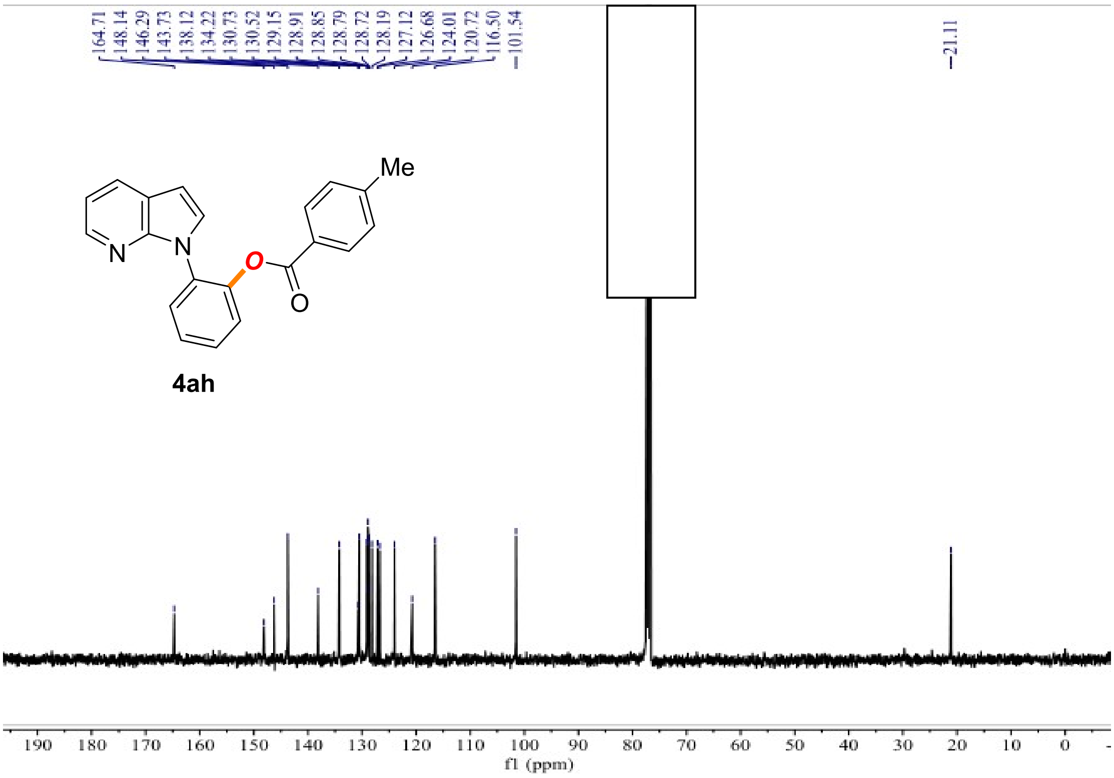
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4ah



4ah

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134.22
130.73
130.52
129.15
128.91
128.85
128.79
128.72
128.19
127.12
126.68
124.01
120.72
116.50
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21.11
Me
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N
O
O
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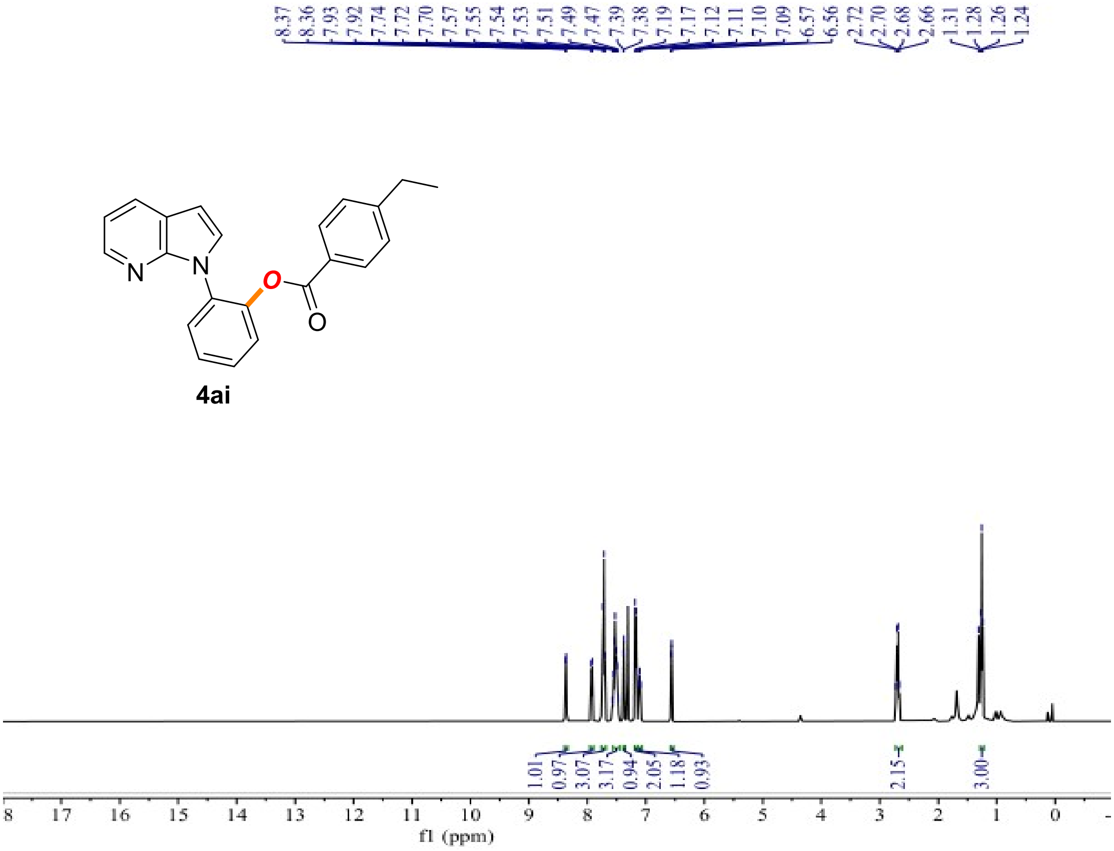
f1 (ppm)



4ai

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7.72
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7.57
7.55
7.54
7.53
7.51
7.49
7.47
7.39
7.38
7.19
7.17
7.12
7.11
7.10
7.09
6.57
6.56
2.72
2.70
2.68
2.66
1.31
1.28
1.26
1.24
N
N
O
O
1.01
0.97
3.07
3.17
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1.18
0.93
2.15
3.00
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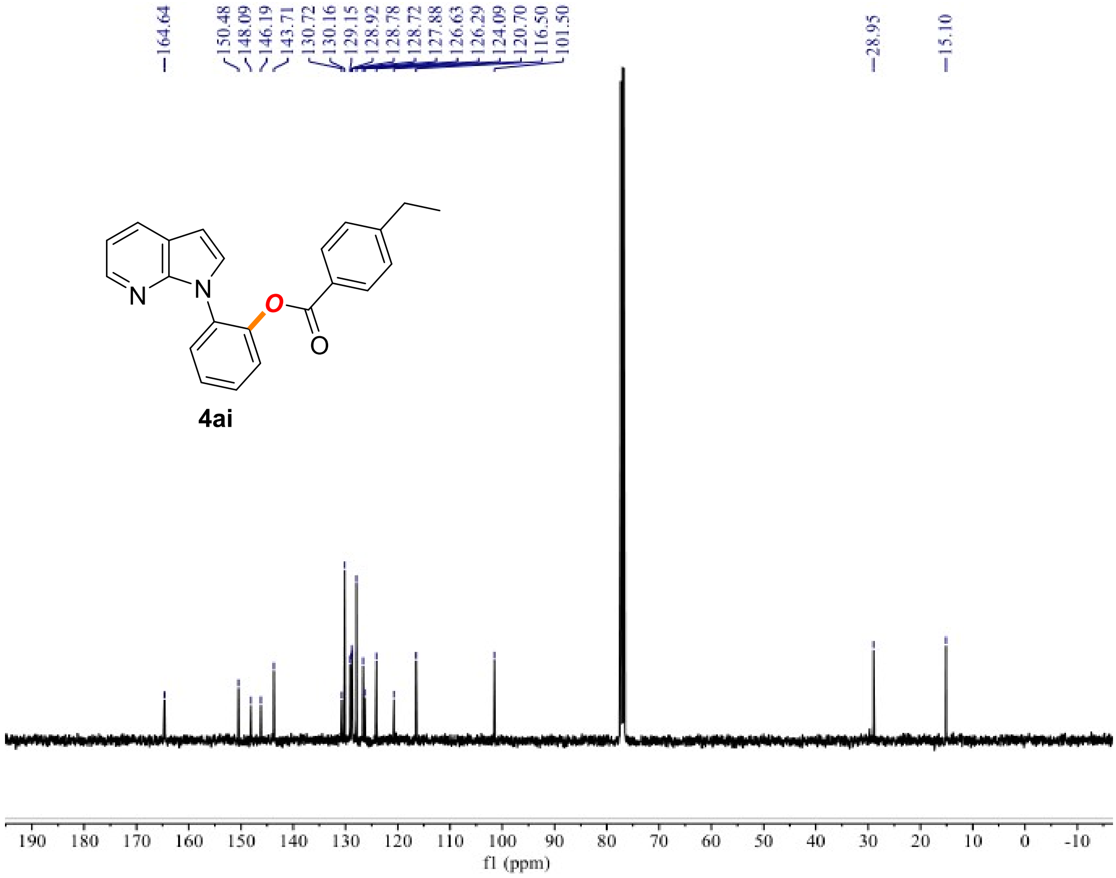
f1 (ppm)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126.63
126.29
124.09
120.70
116.50
101.50
28.95
15.10
N
N
O
O
190
180
170
160
150
140
130
120
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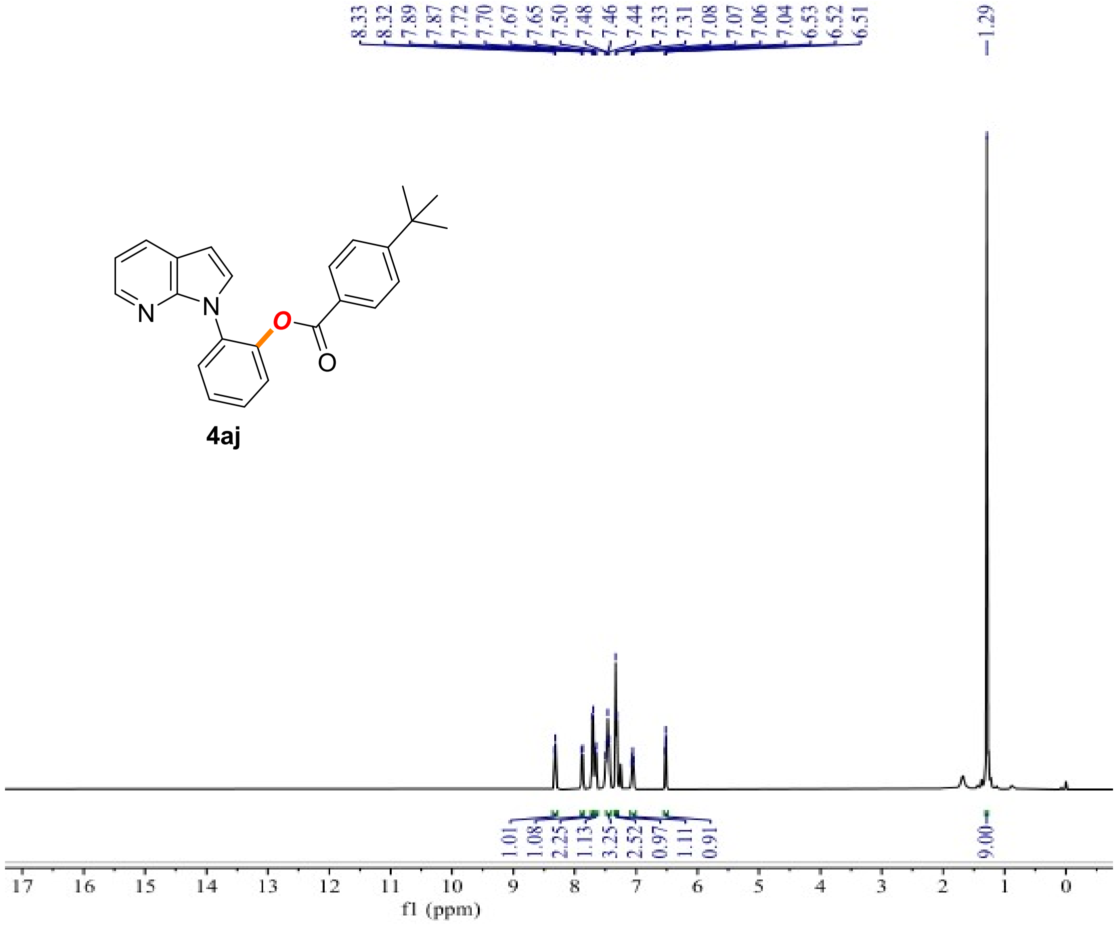
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4ai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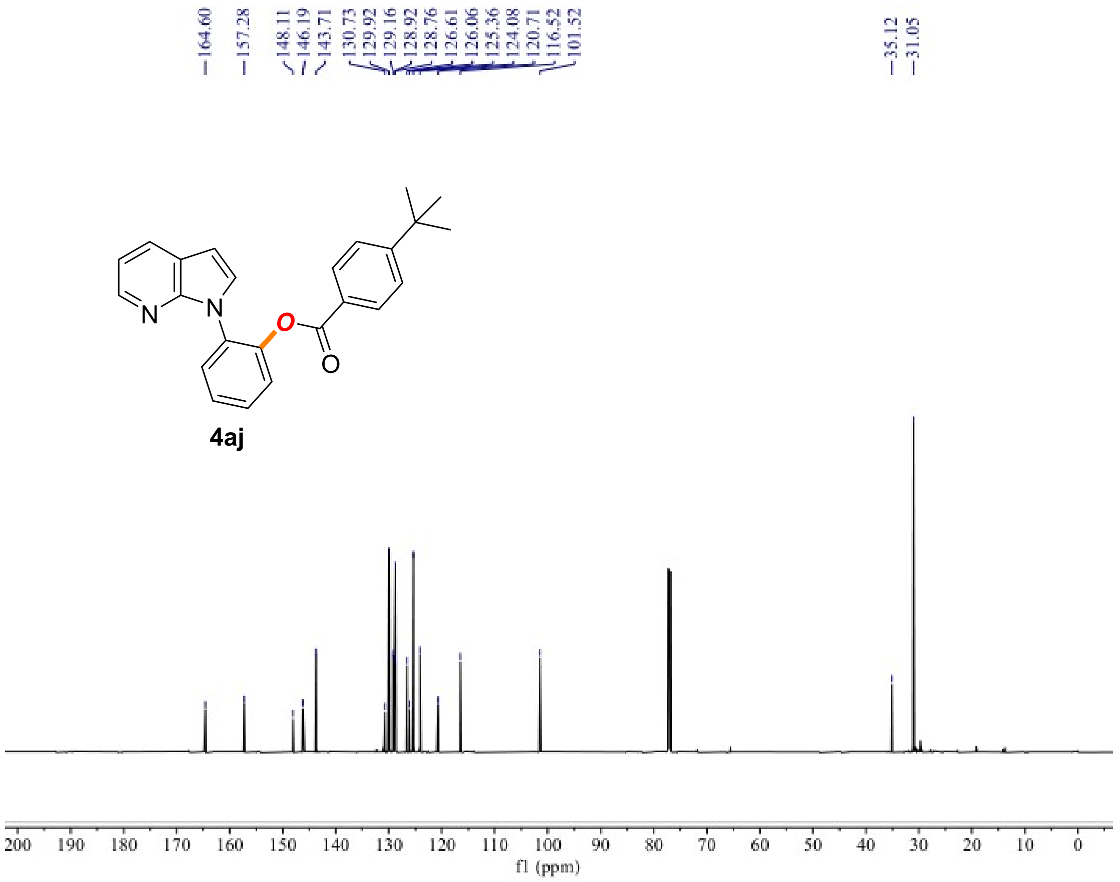
7.46
7.44
7.33
7.31
7.08
7.07
7.06
7.04
6.53
6.52
6.51
1.29
N
N
O
O
1.01
1.08
2.25
1.13
3.25
2.52
0.97
1.11
0.91
9.00
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4aj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128.92
128.76
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126.06
125.36
124.08
120.71
116.52
101.52
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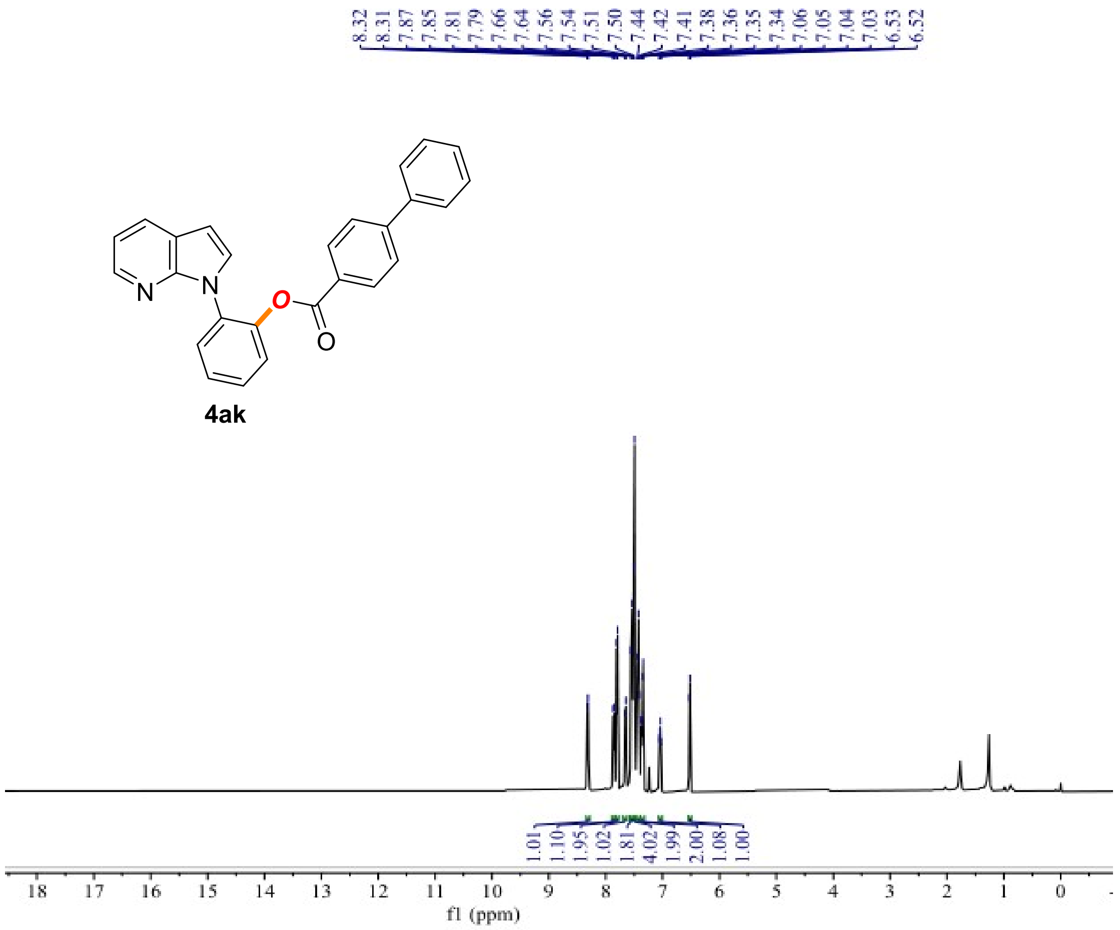
31.05
N
N
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4ak
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7.56
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7.51
7.50
7.44
7.42
7.41
7.38
7.36
7.35
7.34
7.06
7.05
7.04
7.03
6.53
6.52
N
N
O
O
1.01
1.10
1.95
1.02
1.81
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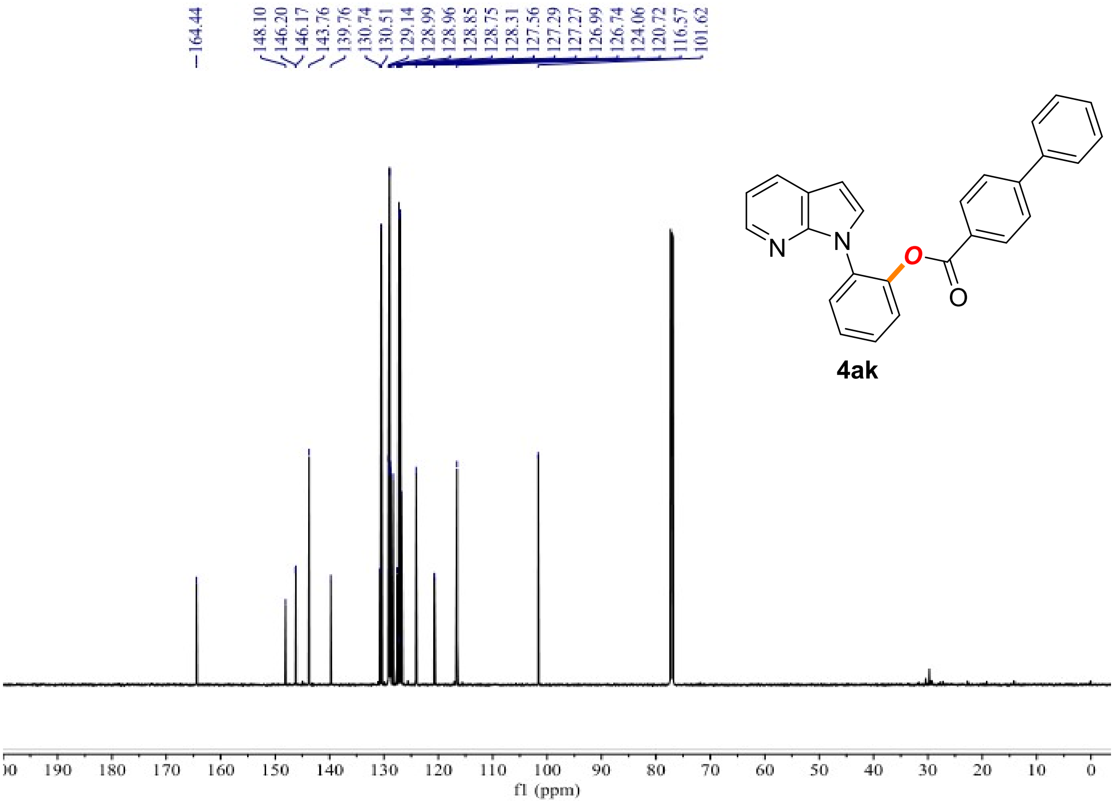
1.99
2.00
1.08
1.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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128.31
127.56
127.29
127.27
126.99
126.74
124.06
120.72
116.57
101.62
O
N
N
O
00
190
180
170
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110
100
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80
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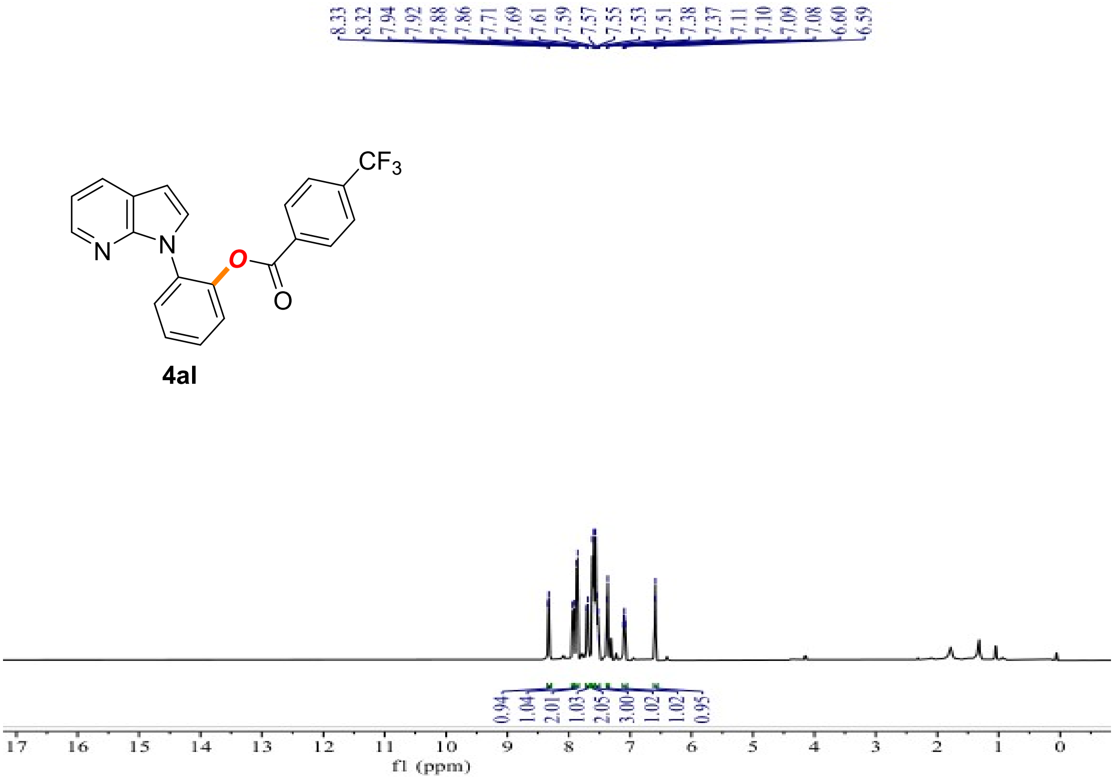
60
50
40
30
20
10
0
f1 (ppm)

4ak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7.59
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7.53
7.51
7.38
7.37
7.11
7.10
7.09
7.08
6.60
6.59
CF3
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N
O
O
0.94
1.04
2.01
1.03
2.05
3.00
1.02
1.02
0.95
17
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11
10
9
8
7
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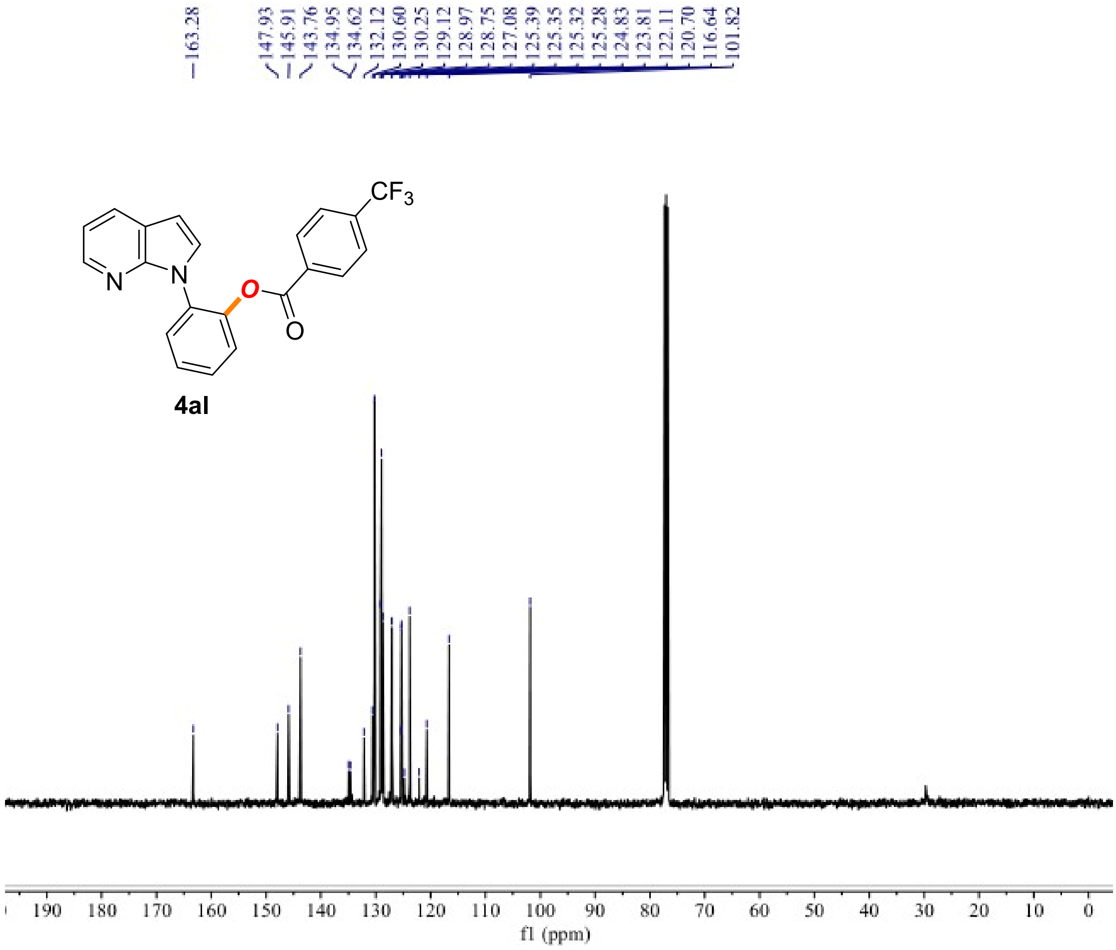
5
4
3
2
1
0
f1 (ppm)

4al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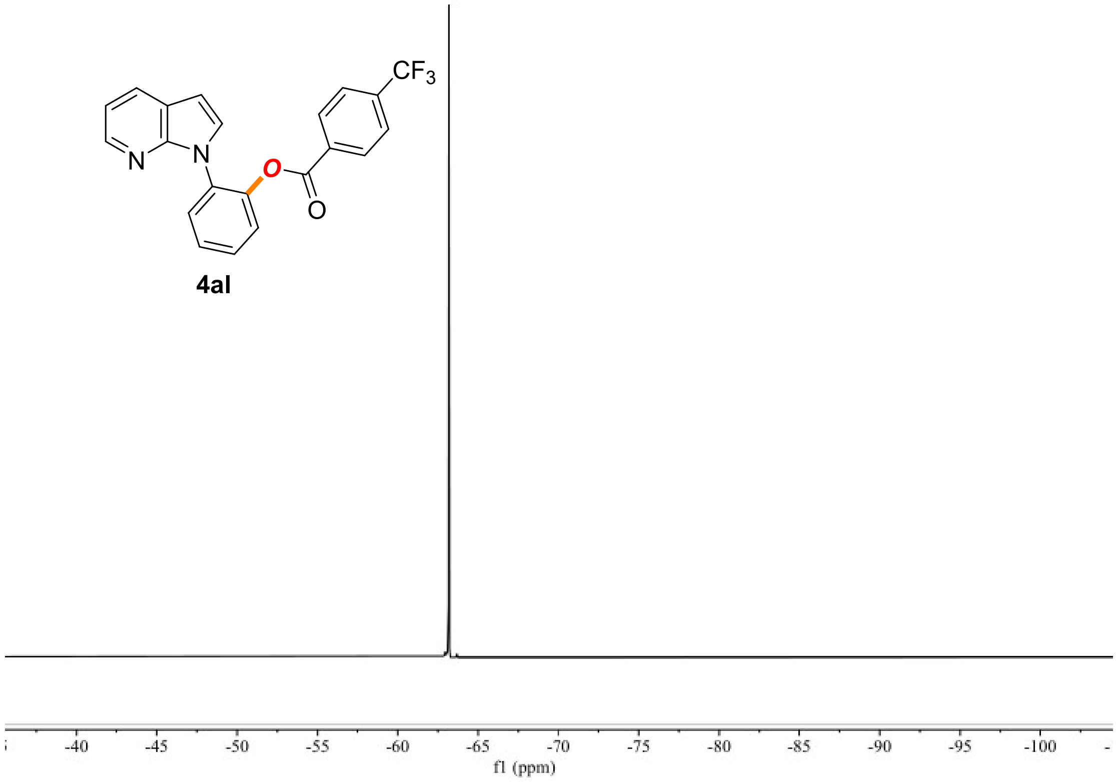
129.12
128.97
128.75
127.08
125.39
125.35
125.32
125.28
124.83
123.81
122.11
120.70
116.64
101.82
N
N
O
O
CF3
4al
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
CF3
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-55
-60
-65
-70
-75
-80
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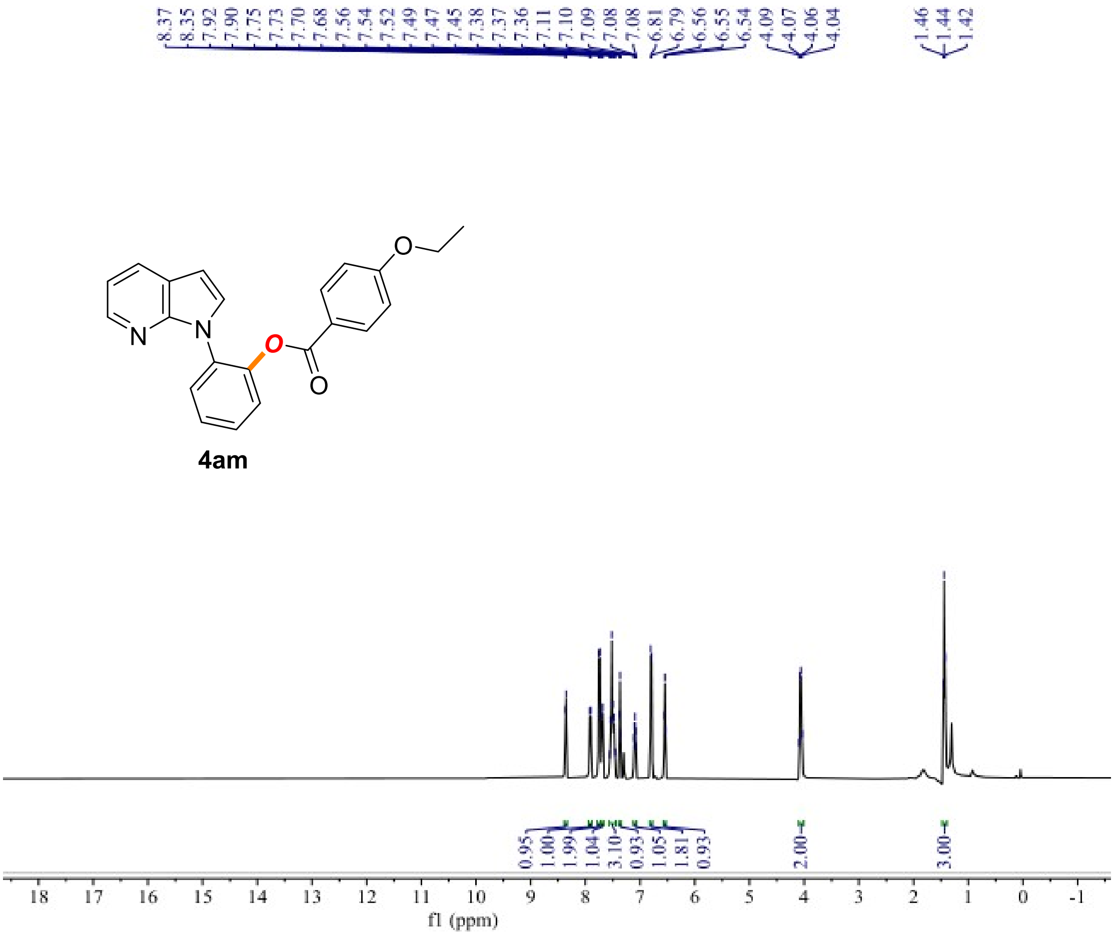
-90
-95
-100
f1 (ppm)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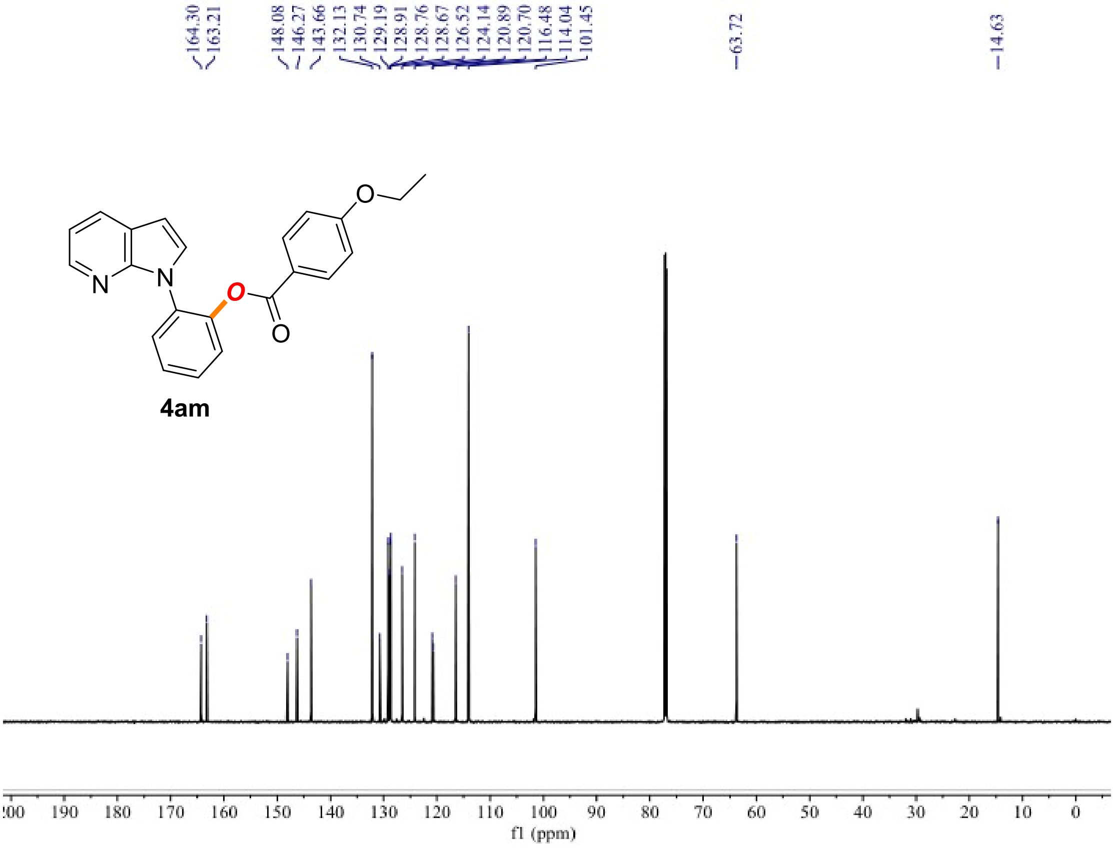
7.52
7.49
7.47
7.45
7.38
7.37
7.36
7.11
7.10
7.09
7.08
7.08
6.81
6.79
6.56
6.55
6.54
4.09
4.07
4.06
4.04
1.46
1.44
1.42
N
N
O
O
O
4am
0.95
1.00
1.99
1.04
3.10
0.93
1.05
1.81
0.93
2.00
3.00
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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146.27
143.66
132.13
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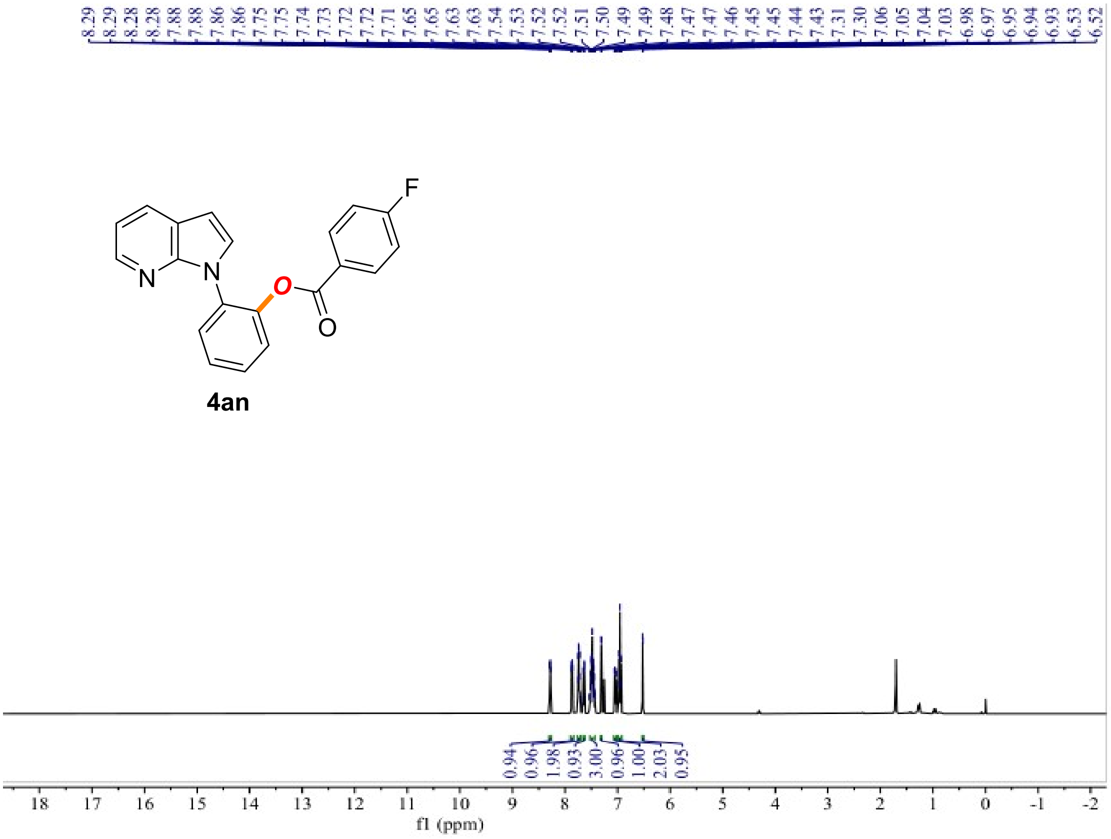
129.19
128.91
128.76
128.67
126.52
124.14
120.89
120.70
116.48
114.04
101.45
63.72
14.63
N
N
O
O
O
4am
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.28
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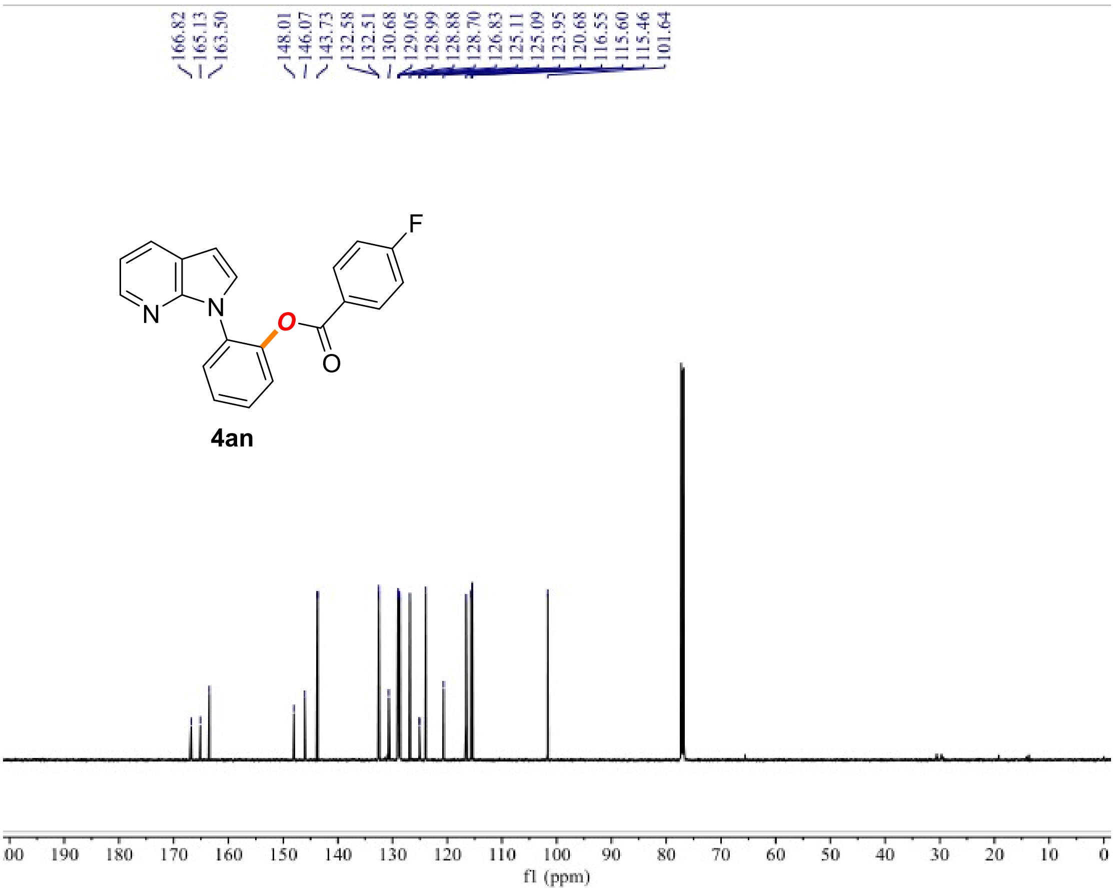
7.88
7.86
7.86
7.75
7.75
7.74
7.73
7.72
7.72
7.71
7.65
7.65
7.63
7.63
7.54
7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.31
7.30
7.06
7.05
7.04
7.03
6.98
6.97
6.95
6.94
6.93
6.53
6.52
F
N
N
O
O
4an
0.94
0.96
1.98
0.93
3.00
0.96
1.00
2.03
0.95
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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163.50
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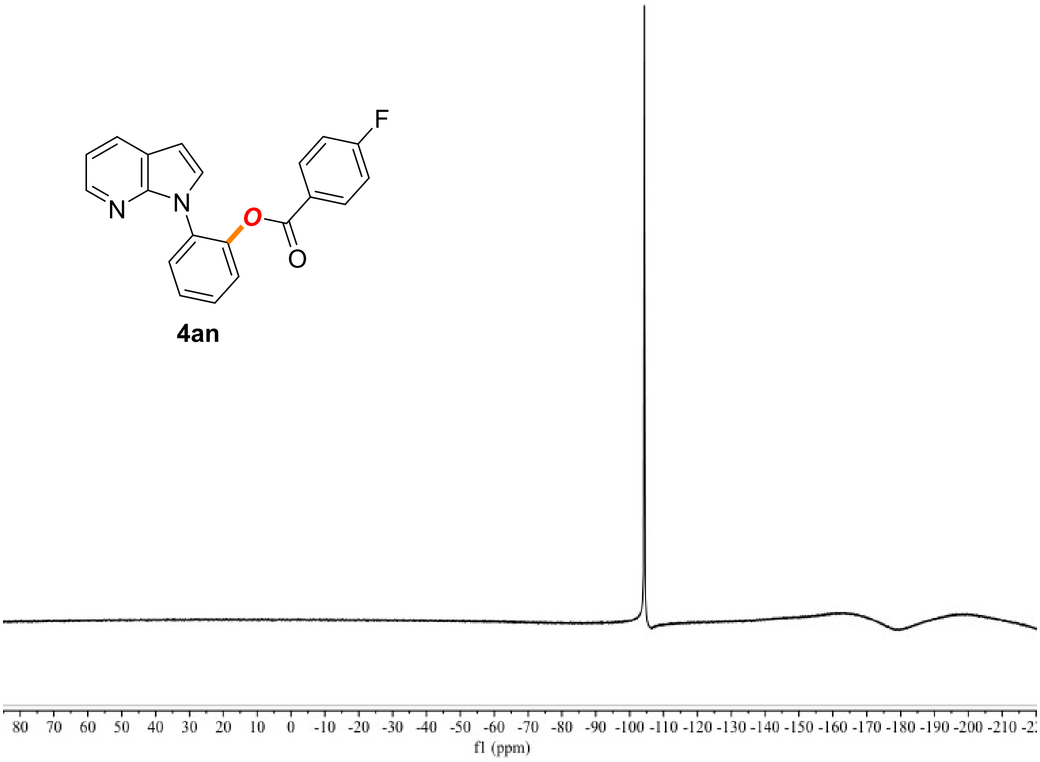
146.07
143.73
132.58
132.51
130.68
129.05
128.99
128.88
128.70
126.83
125.11
125.09
123.95
120.68
116.55
115.60
115.46
101.64
F
N
N
O
O
4an
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

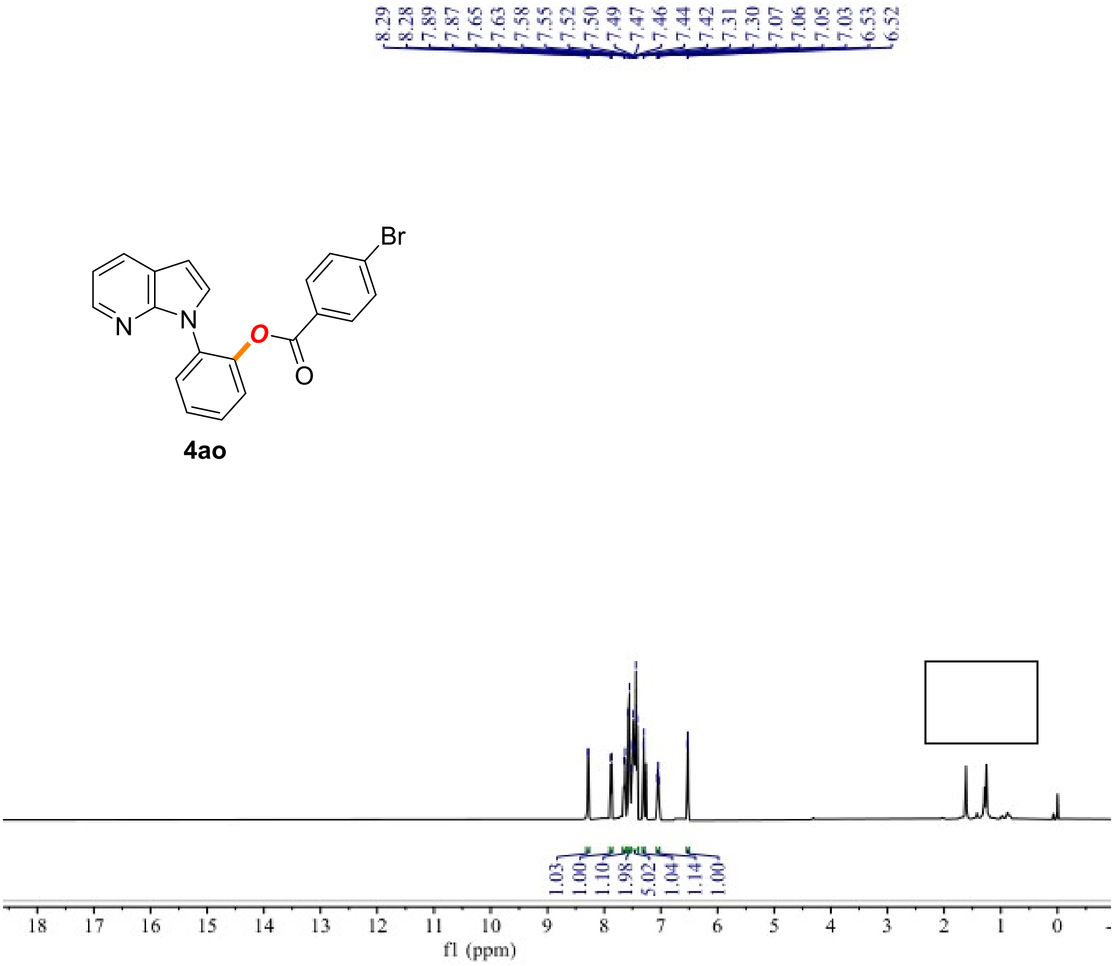
F
N
N
O
O

4an


80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Br
N
N
O
O

4ao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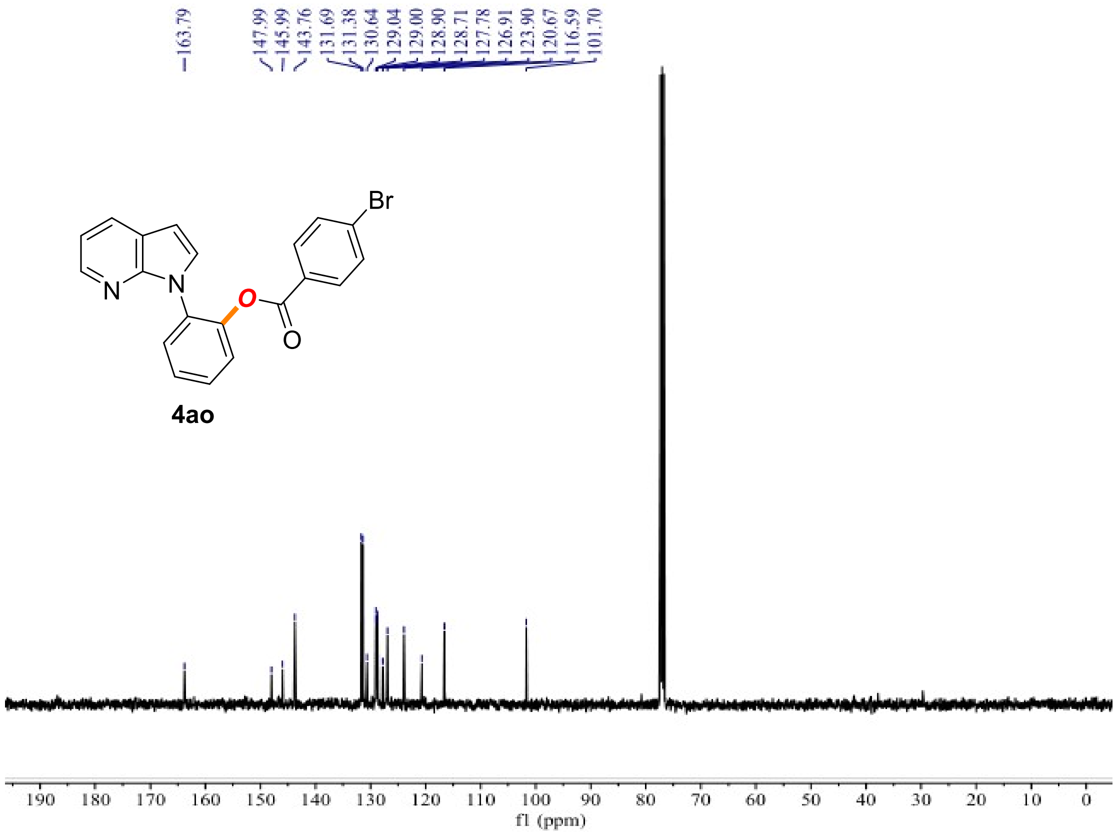
8.28
7.89
7.87
7.65
7.63
7.58
7.55
7.52
7.50
7.49
7.47
7.46
7.44
7.42
7.31
7.30
7.07
7.06
7.05
7.03
6.53
6.52
1.03
1.00
1.10
1.98
5.02
1.04
1.14
1.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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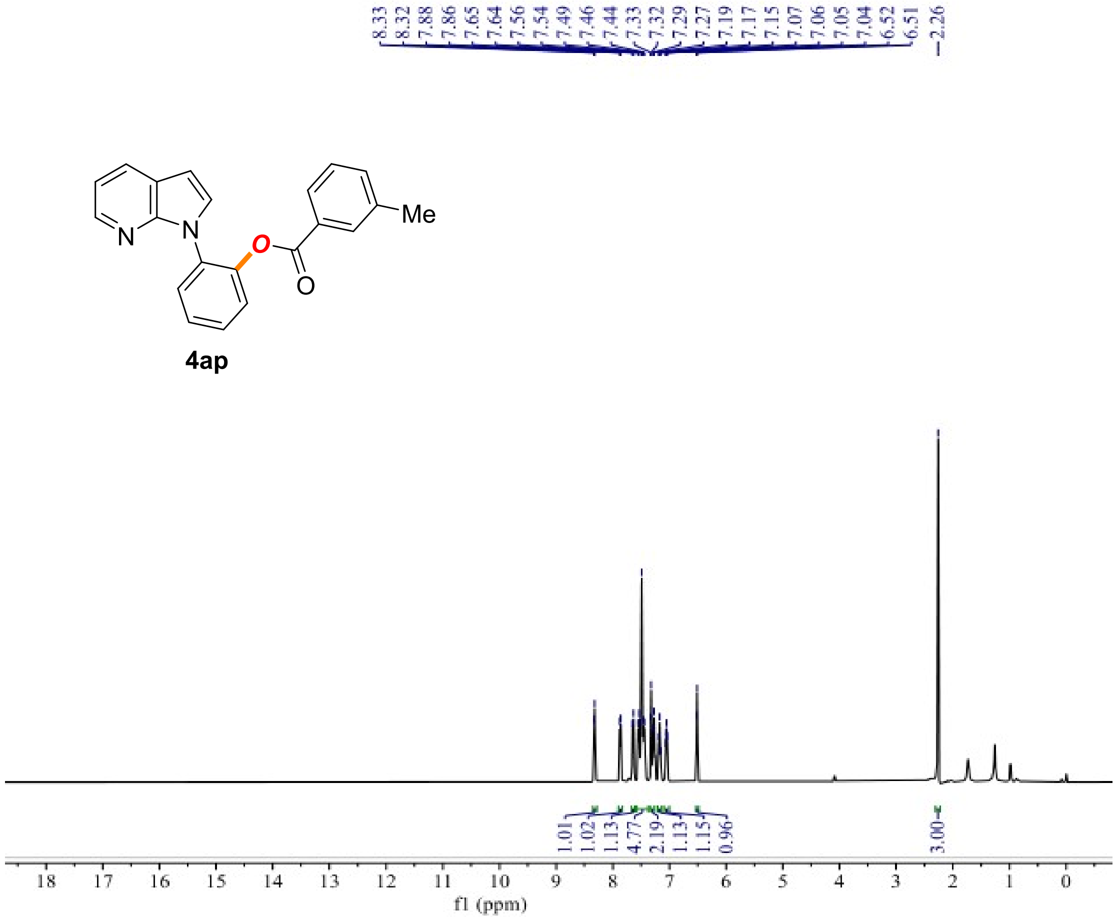
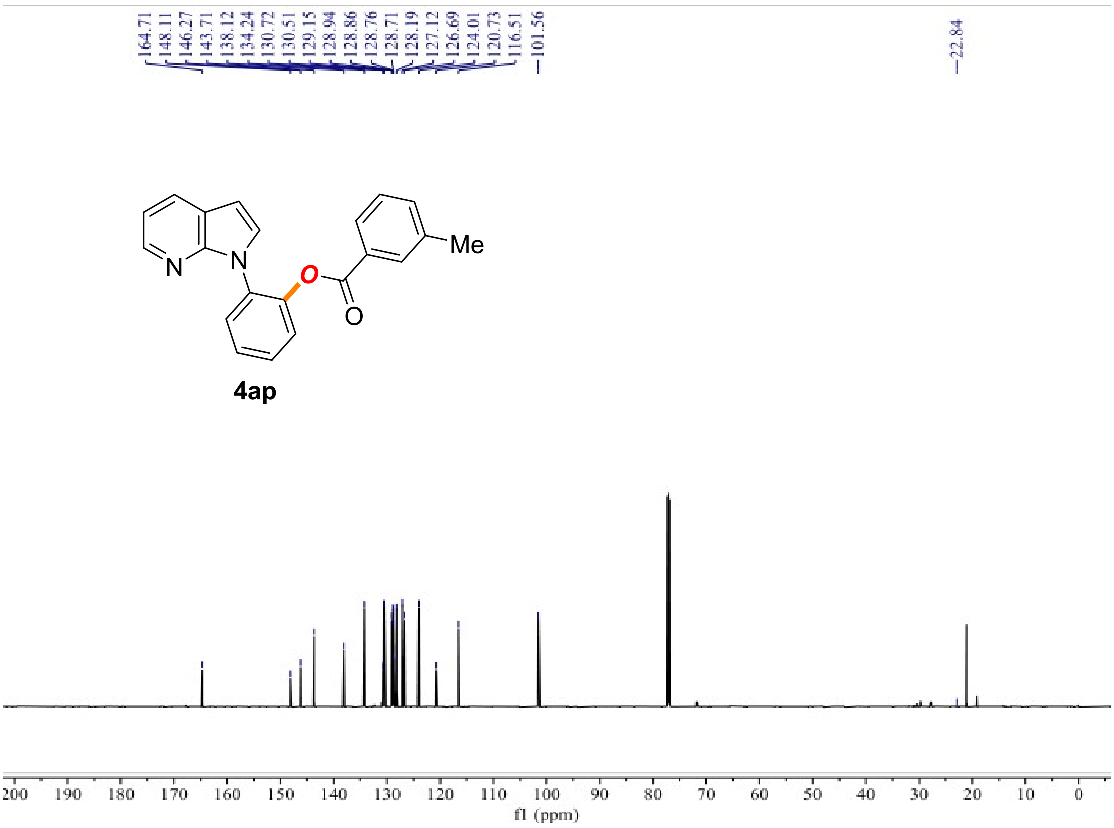
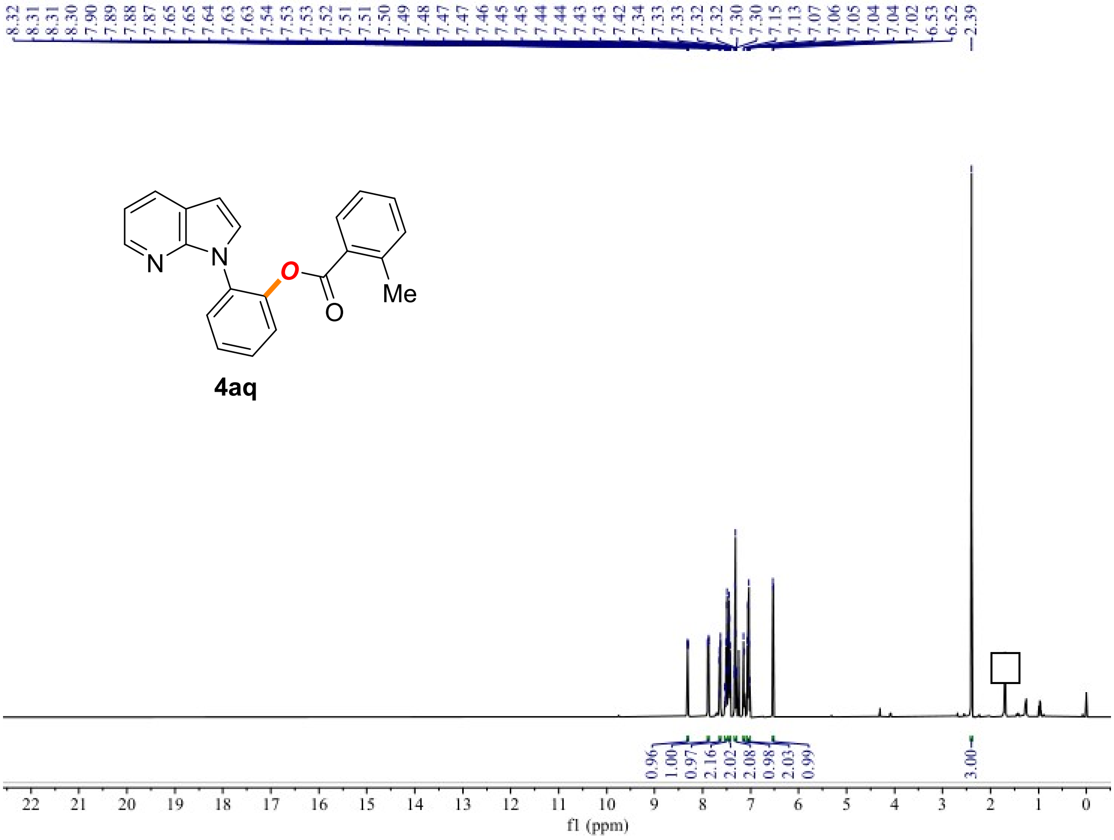
147.99
145.99
143.76
131.69
131.38
130.64
129.04
129.00
128.90
128.71
127.78
126.91
123.90
120.67
116.59
101.70
Br
N
N
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4ao


8.33
8.32
7.88
7.86
7.65
7.64
7.56
7.54
7.49
7.46
7.44
7.33
7.32
7.29
7.27
7.19
7.17
7.15
7.07
7.06
7.05
7.04
6.52
6.51
2.26
Me
N
N
O
O
1.01
1.02
1.13
4.77
2.19
1.13
1.15
0.96
3.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

4ap


164.71
148.11
146.27
143.71
138.12
134.24
130.72
130.51
129.15
128.94
128.86
128.76
128.71
128.19
127.12
126.69
124.01
120.73
116.51
101.56
22.84
N
N
O
O
Me
4ap
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.31
8.31
8.30
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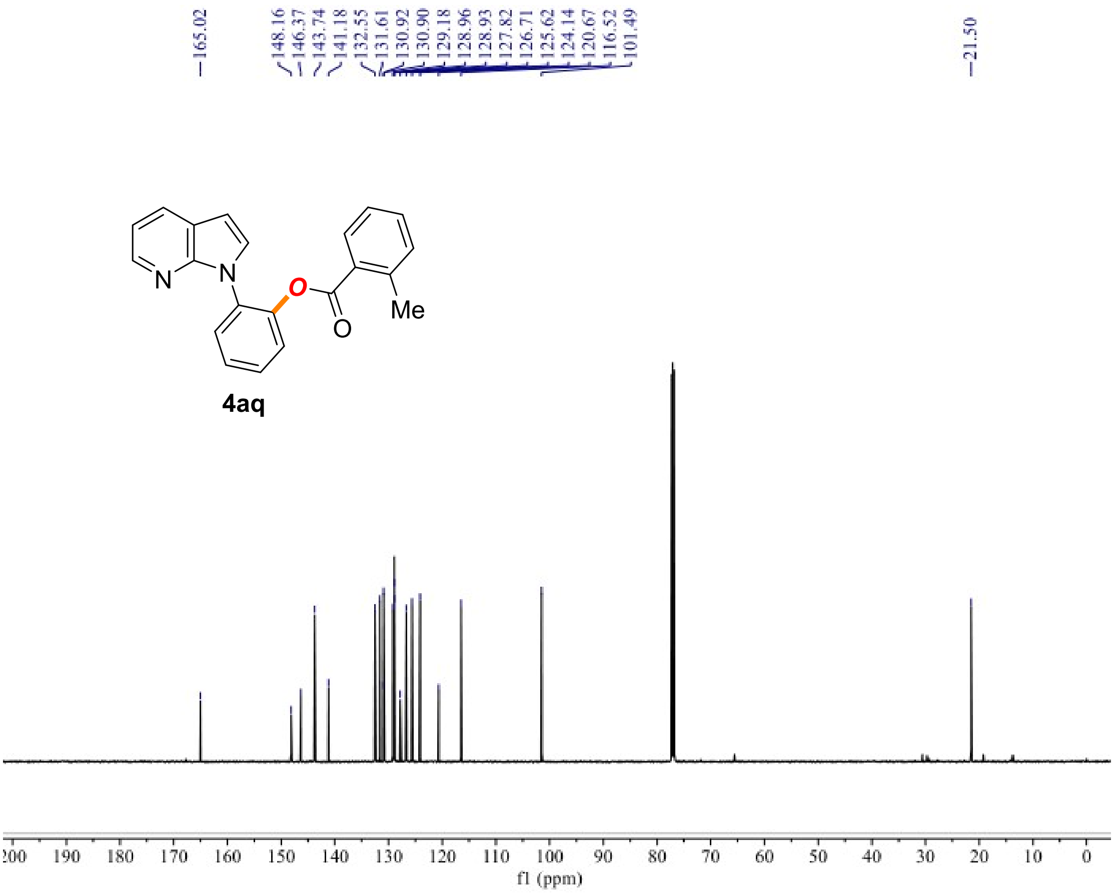
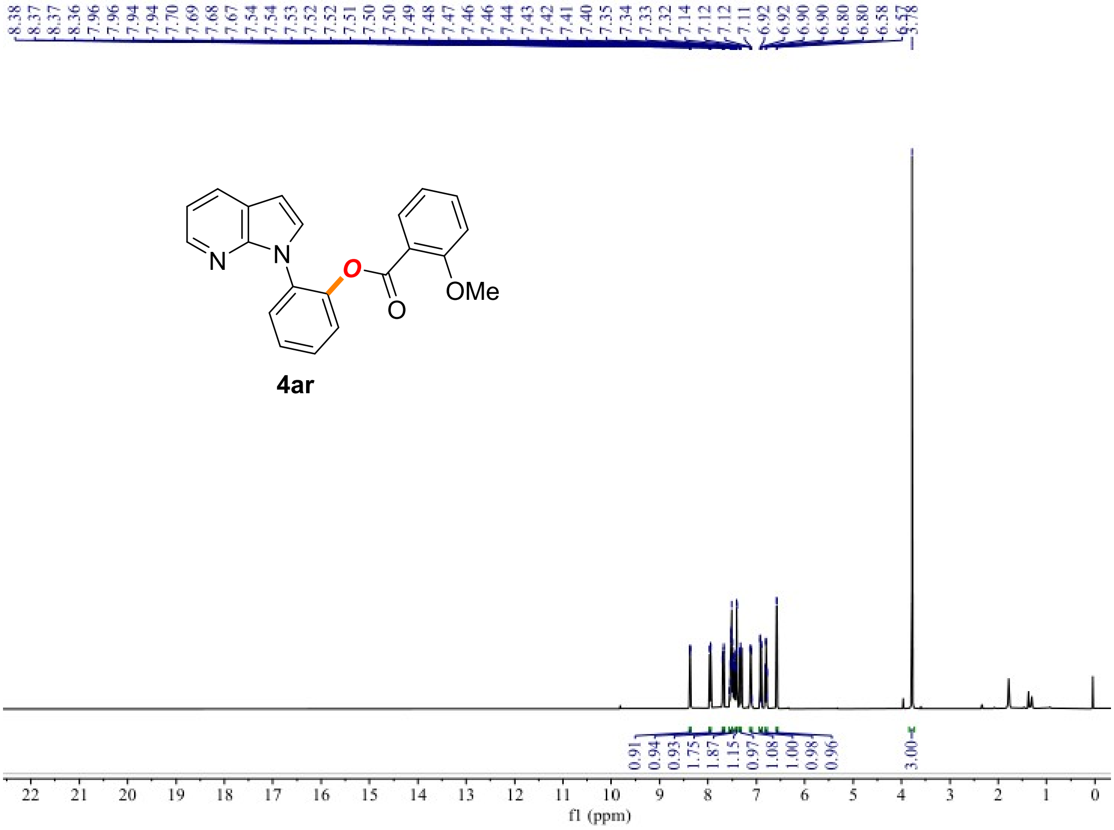
7.89
7.88
7.87
7.65
7.65
7.64
7.63
7.63
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.34
7.33
7.33
7.32
7.32
7.30
7.30
7.15
7.13
7.07
7.06
7.05
7.04
7.04
7.02
6.53
6.52
2.39
N
N
O
O
Me
4aq
0.96
1.00
0.97
2.16
2.02
2.08
0.98
2.03
0.99
3.00
22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


165.02
148.16
146.37
143.74
141.18
132.55
131.61
130.92
130.90
129.18
128.96
128.93
127.82
126.71
125.62
124.14
120.67
116.52
101.49
21.50
N
N
O
O
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4aq


8.38
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7.96
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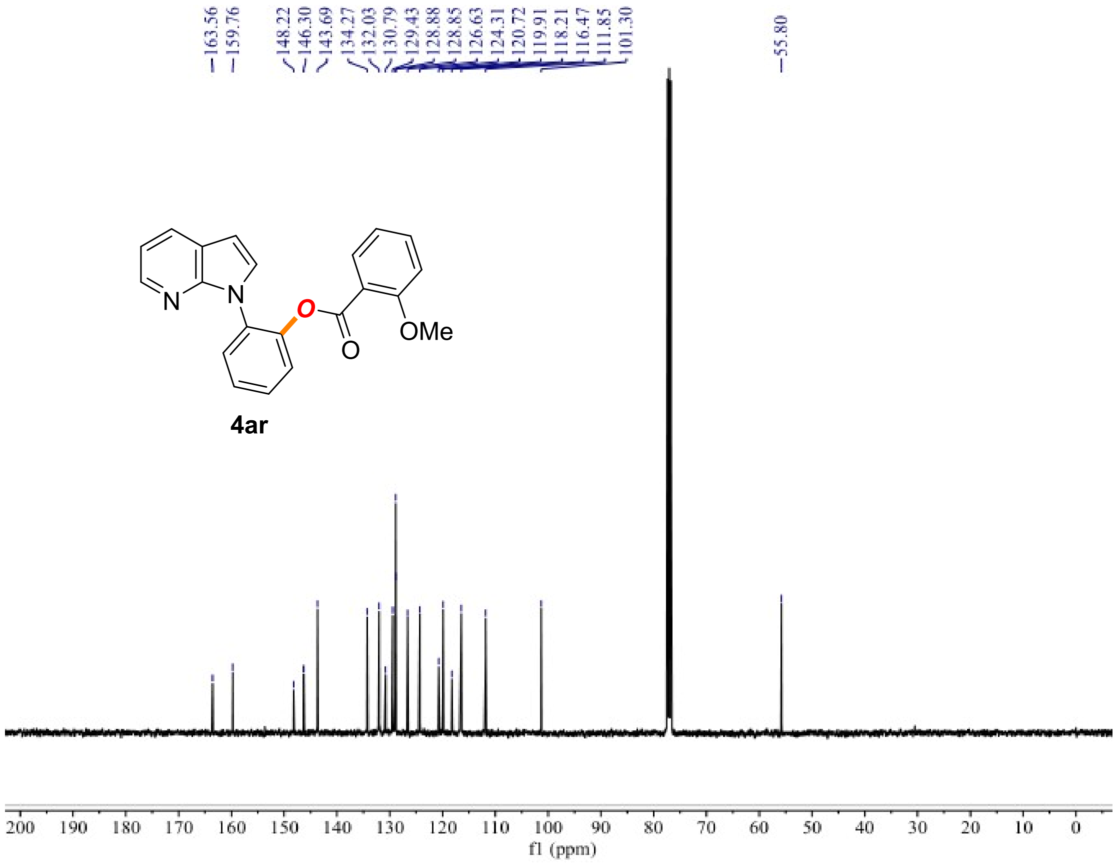
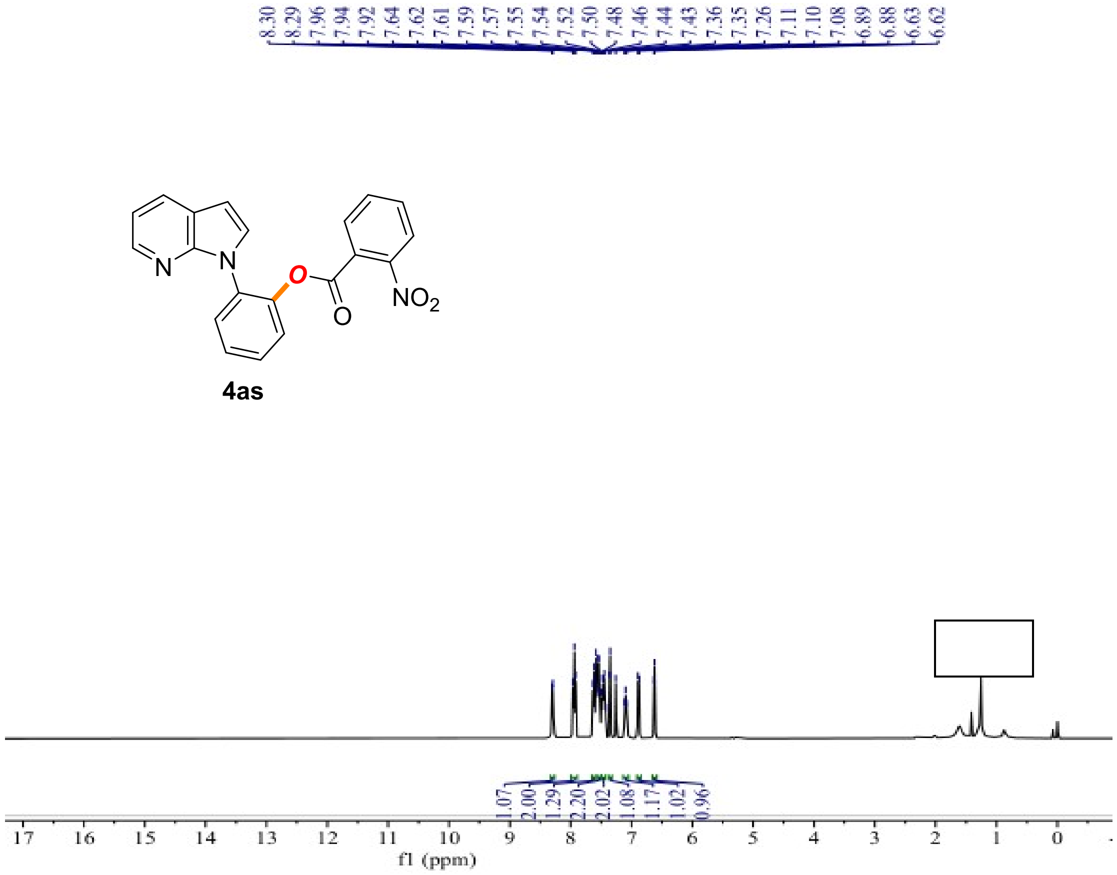
7.68
7.67
7.54
7.54
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.44
7.43
7.42
7.41
7.40
7.35
7.34
7.33
7.32
7.14
7.12
7.12
7.11
6.92
6.92
6.90
6.90
6.80
6.80
6.58
6.57
3.78
N
N
O
O
OMe
0.91
0.94
0.93
1.75
1.87
1.15
0.97
1.08
1.00
0.98
0.96
3.00
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

4ar


163.56
159.76
148.22
146.30
143.69
134.27
132.03
130.79
129.43
128.88
128.85
126.63
124.31
120.72
119.91
118.21
116.47
111.85
101.30
55.80
N
N
O
O
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4ar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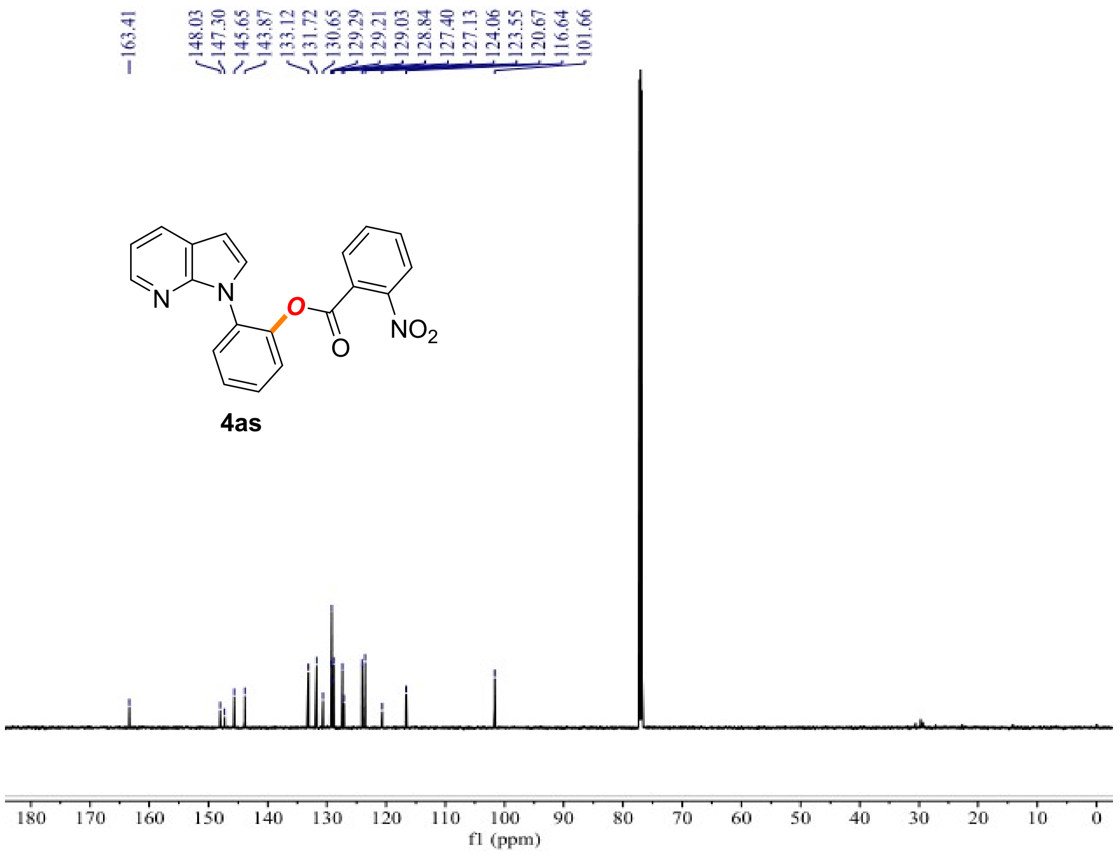
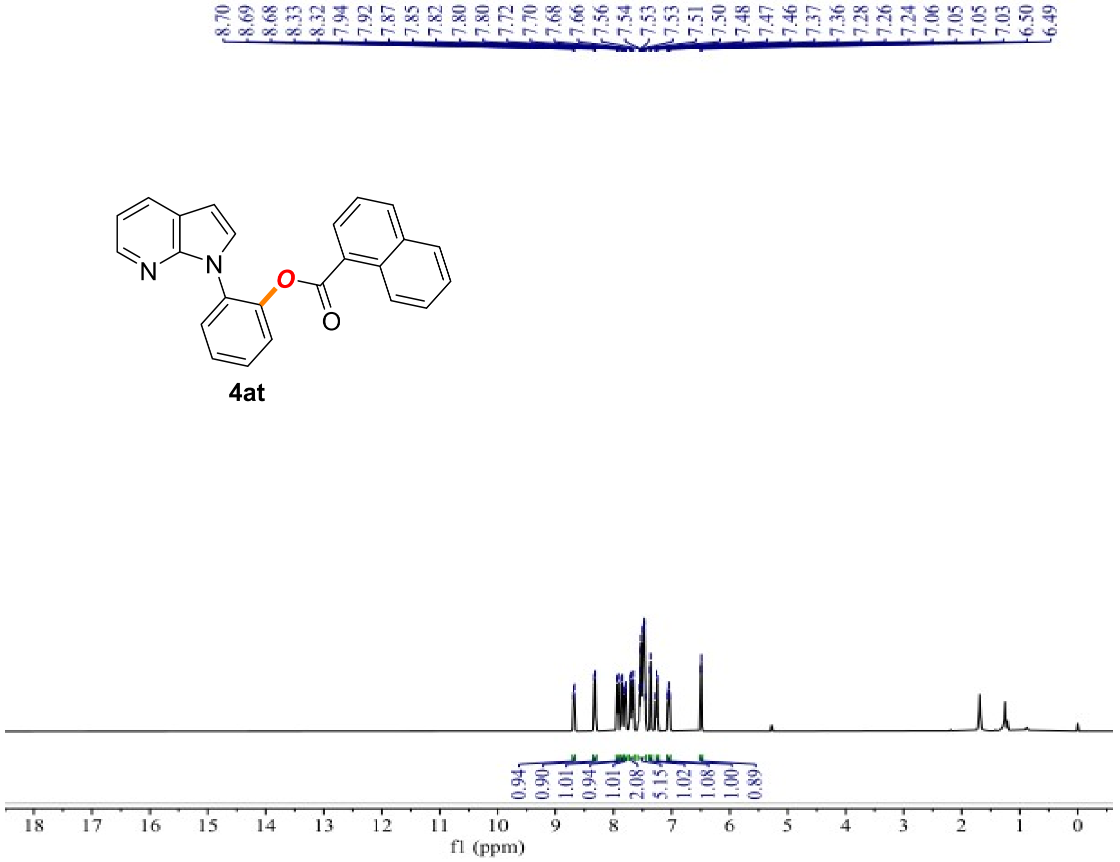
8.29
7.96
7.94
7.92
7.64
7.62
7.61
7.59
7.57
7.55
7.54
7.52
7.50
7.48
7.46
7.44
7.43
7.36
7.35
7.26
7.11
7.10
7.08
6.89
6.88
6.63
6.62
N
N
O
O
NO2
1.07
2.00
1.29
2.20
2.02
1.08
1.17
1.02
0.96
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

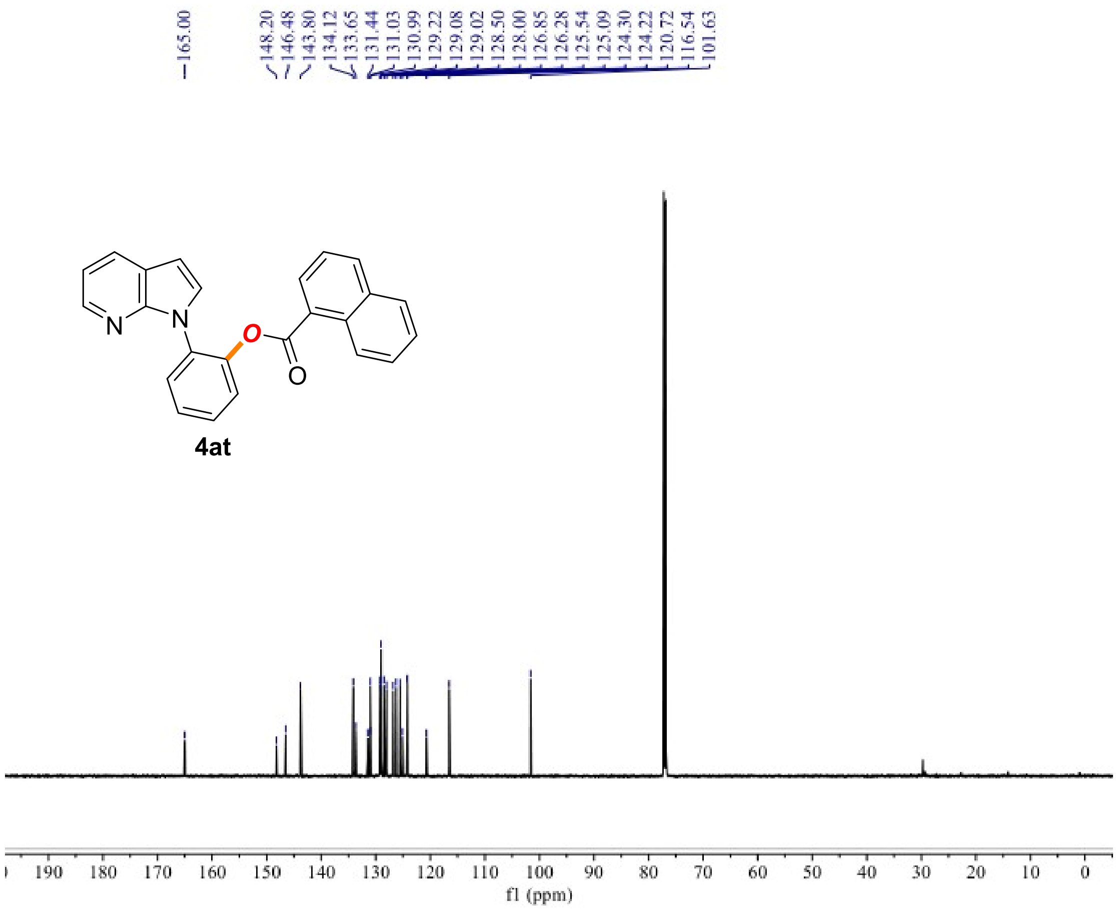
4as


163.41
148.03
147.30
145.65
143.87
133.12
131.72
130.65
129.29
129.21
129.03
128.84
127.40
127.13
124.06
123.55
120.67
116.64
101.66
N
N
O
O
NO_2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4as


8.70
8.69
8.68
8.33
8.32
7.94
7.92
7.87
7.85
7.82
7.80
7.80
7.72
7.70
7.68
7.66
7.56
7.54
7.53
7.53
7.51
7.50
7.48
7.47
7.46
7.37
7.36
7.28
7.26
7.24
7.06
7.05
7.05
7.03
6.50
6.49
N
N
O
O
0.94
0.90
1.01
0.94
1.01
2.08
5.15
1.02
1.08
1.00
0.89
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

4at


4at

165.00
148.20
146.48
143.80
134.12
133.65
131.44
131.03
130.99
129.22
129.08
129.02
128.50
128.00
126.85
126.28
125.54
125.09
124.30
124.22
120.72
116.54
101.63
N
N
O
O
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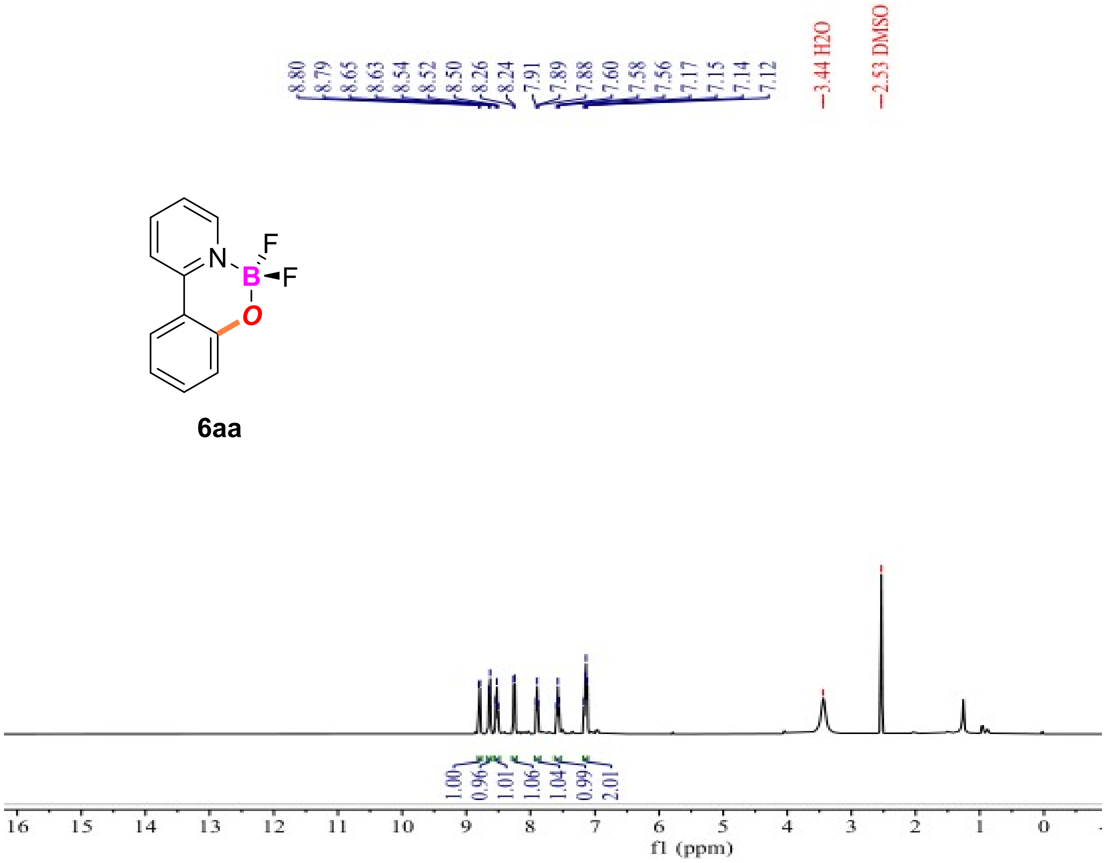
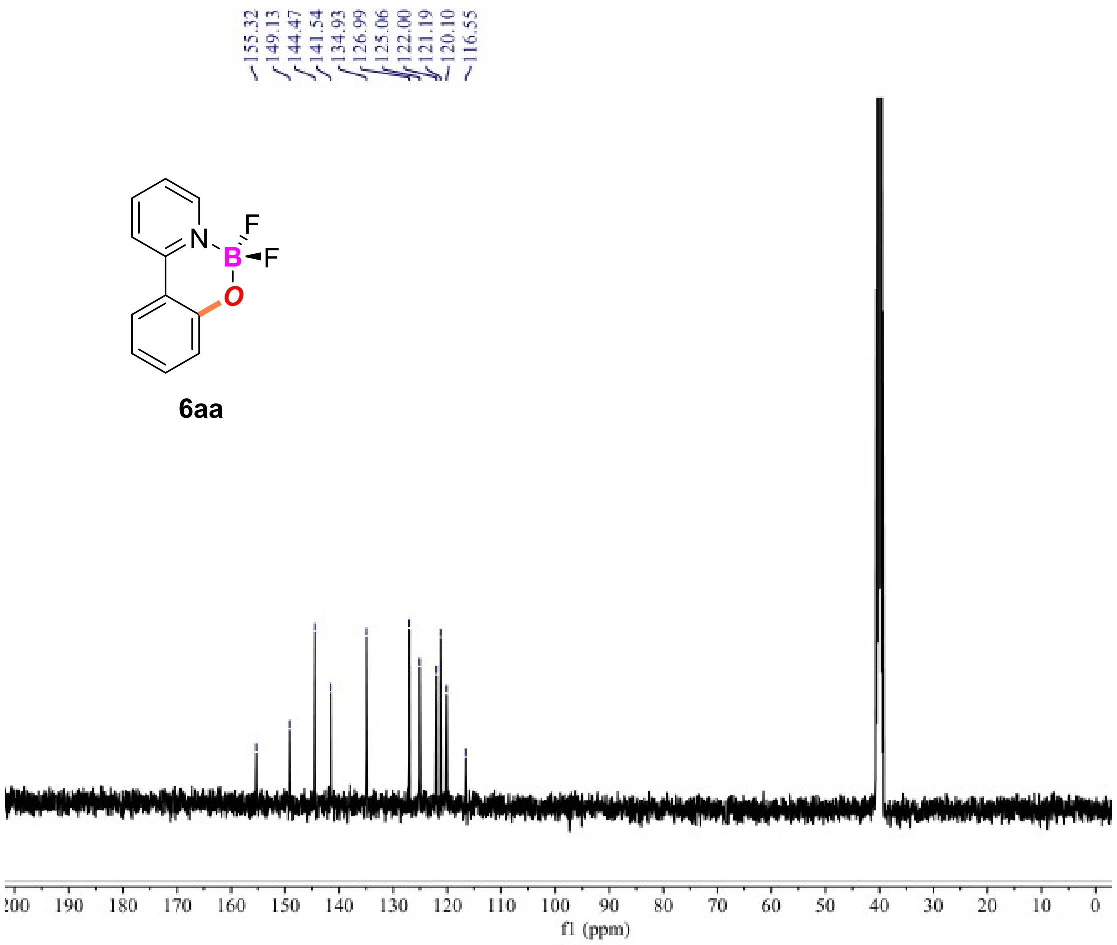
f1 (ppm)


6aa

8.80
8.79
8.65
8.63
8.54
8.52
8.50
8.26
8.24
7.91
7.89
7.88
7.60
7.58
7.56
7.17
7.15
7.14
7.12
3.44 H2O
2.53 DMSO
N
B
F
F
O
1.00
0.96
1.01
1.06
1.04
0.99
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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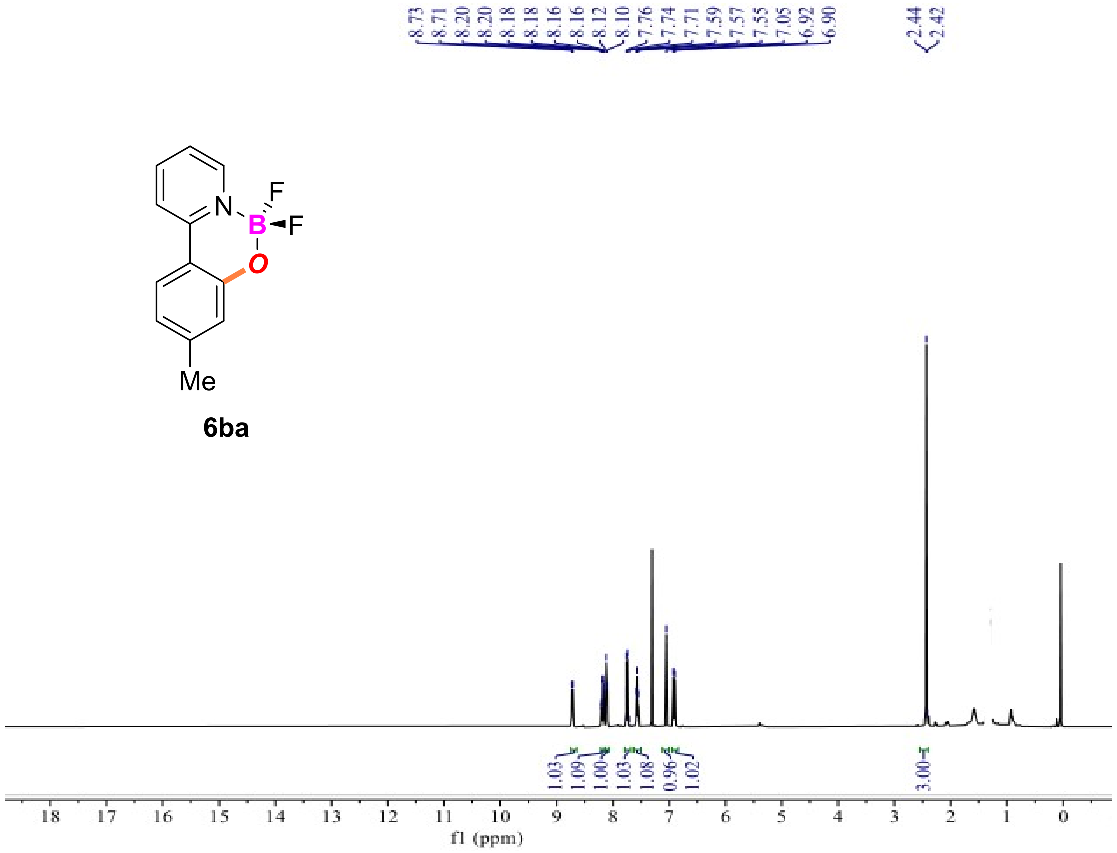
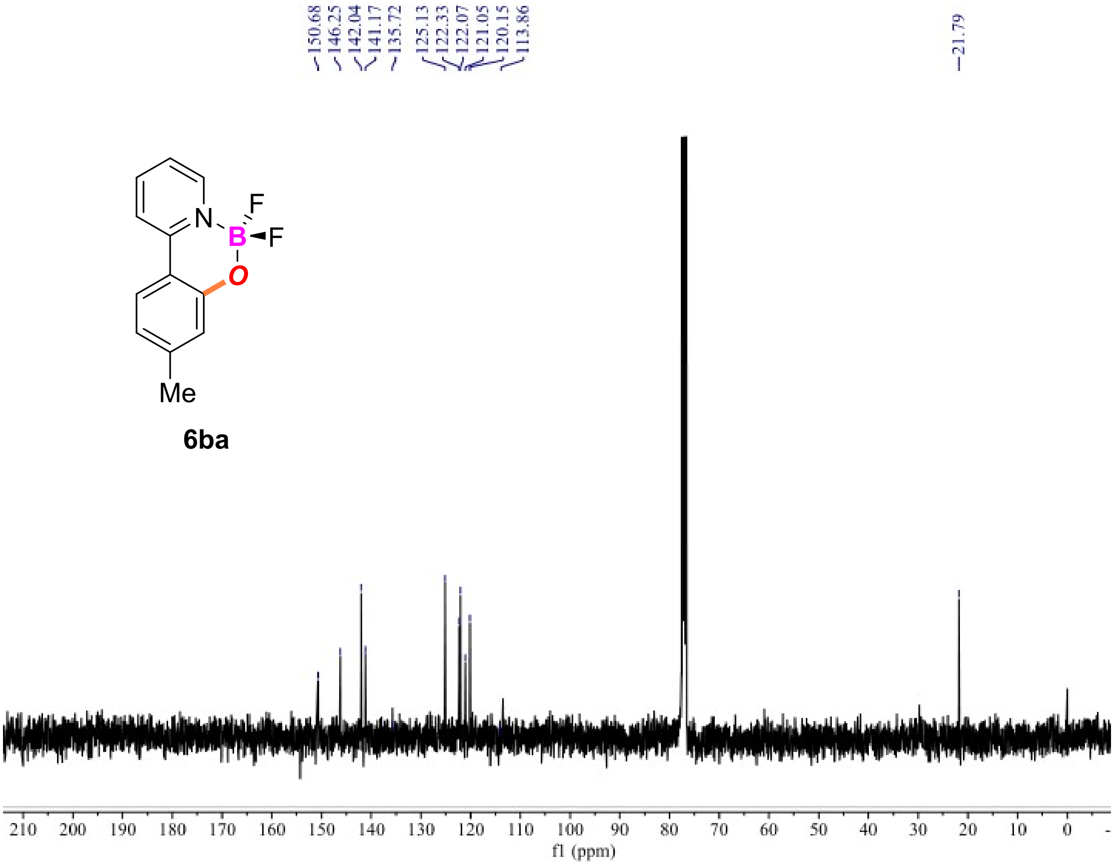
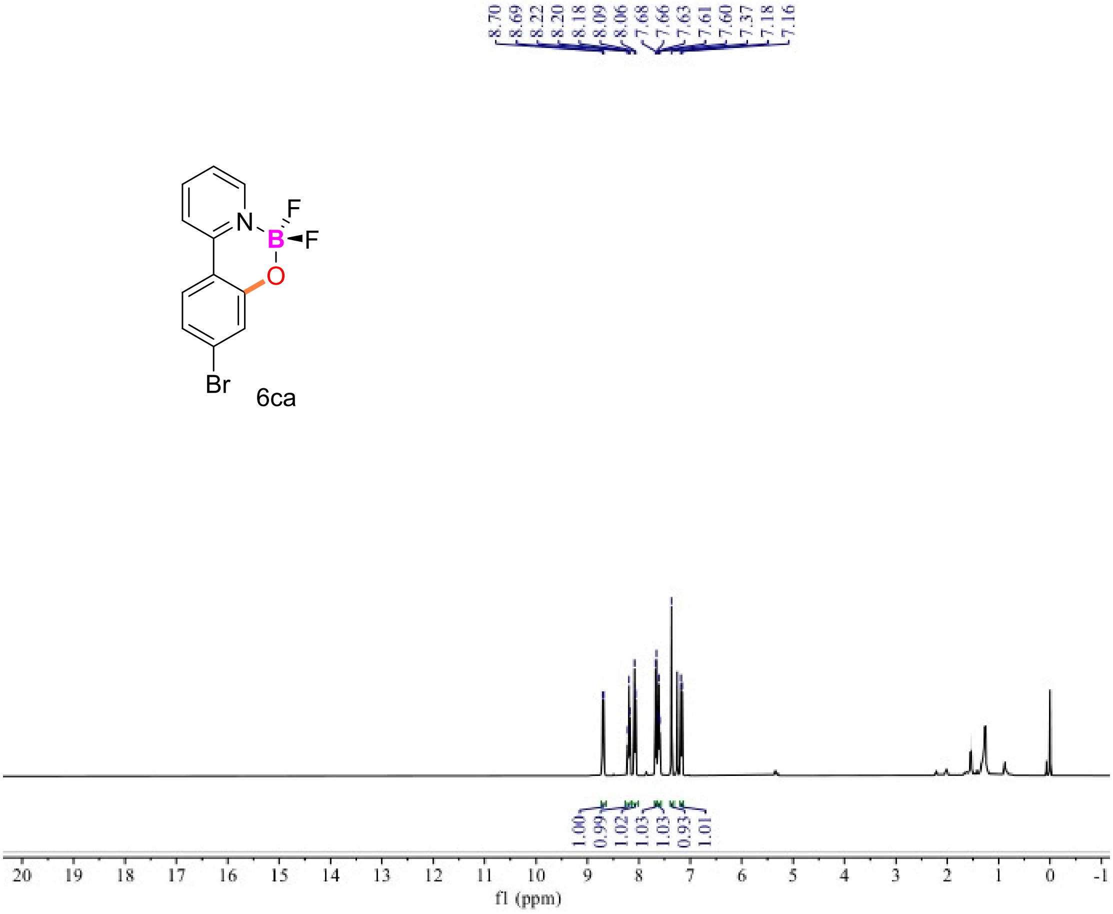
144.47
141.54
134.93
126.99
125.06
122.00
121.19
120.10
116.55
N
B
F
F
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

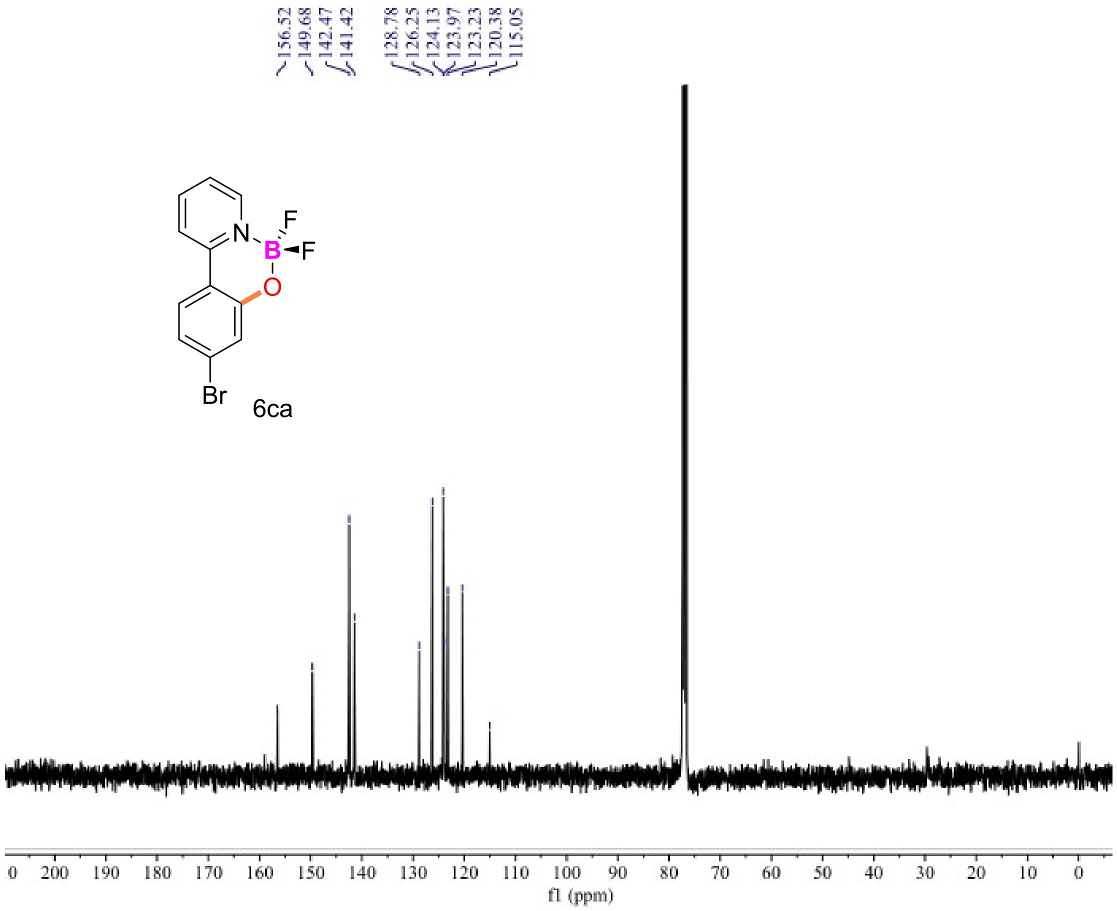
6aa


8.73
8.71
8.20
8.20
8.18
8.18
8.16
8.16
8.12
8.10
7.76
7.74
7.71
7.59
7.57
7.55
7.05
6.92
6.90
2.44
2.42
N
B
F
F
O
Me
1.03
1.09
1.00
1.03
1.08
0.96
1.02
3.00
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

6ba


150.68
146.25
142.04
141.17
135.72
125.13
122.33
122.07
121.05
120.15
113.86
21.79
N
B
F
F
O
Me
6ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.70
8.69
8.22
8.20
8.18
8.09
8.06
7.68
7.66
7.63
7.61
7.60
7.37
7.18
7.16
N
B
F
F
O
Br
6ca
1.00
0.99
1.02
1.03
1.03
0.93
1.01
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


156.52
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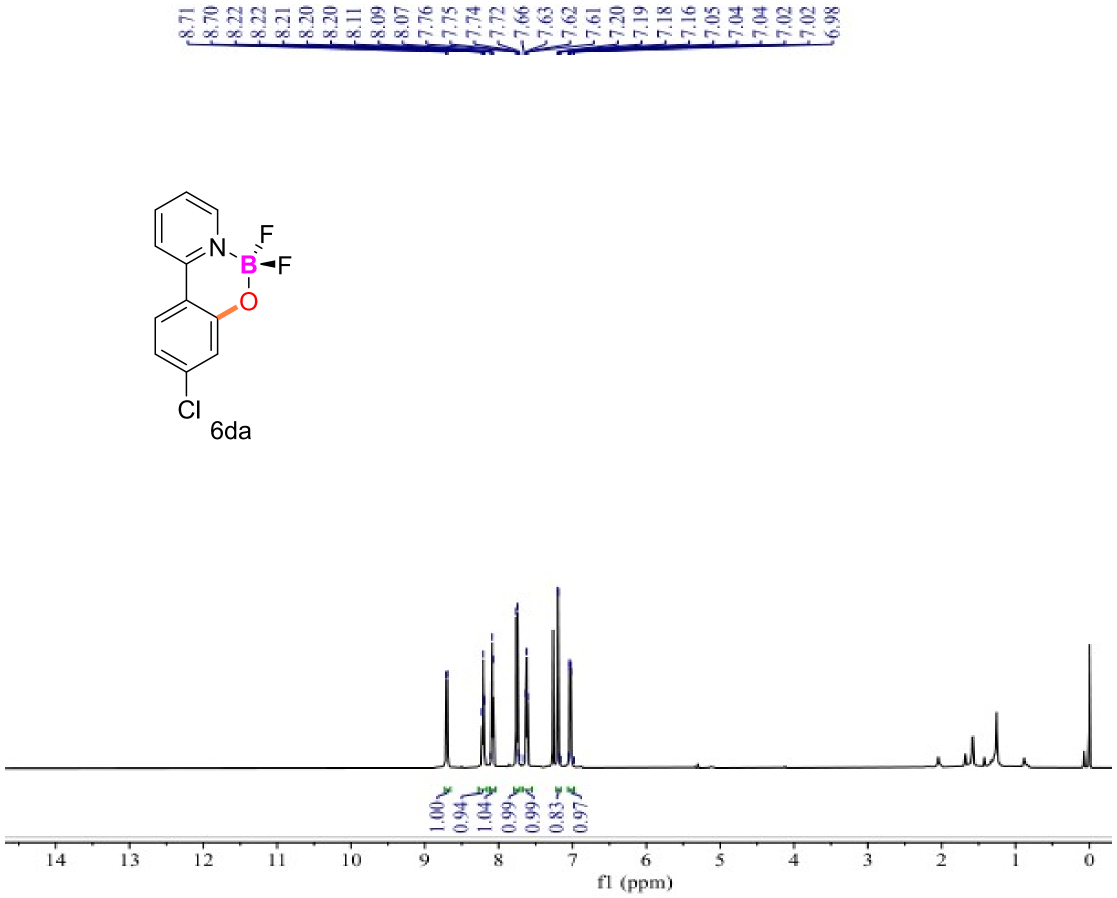
142.47
141.42
128.78
126.25
124.13
123.97
123.23
120.38
115.05
N
B
F
F
O
Br
6ca
0 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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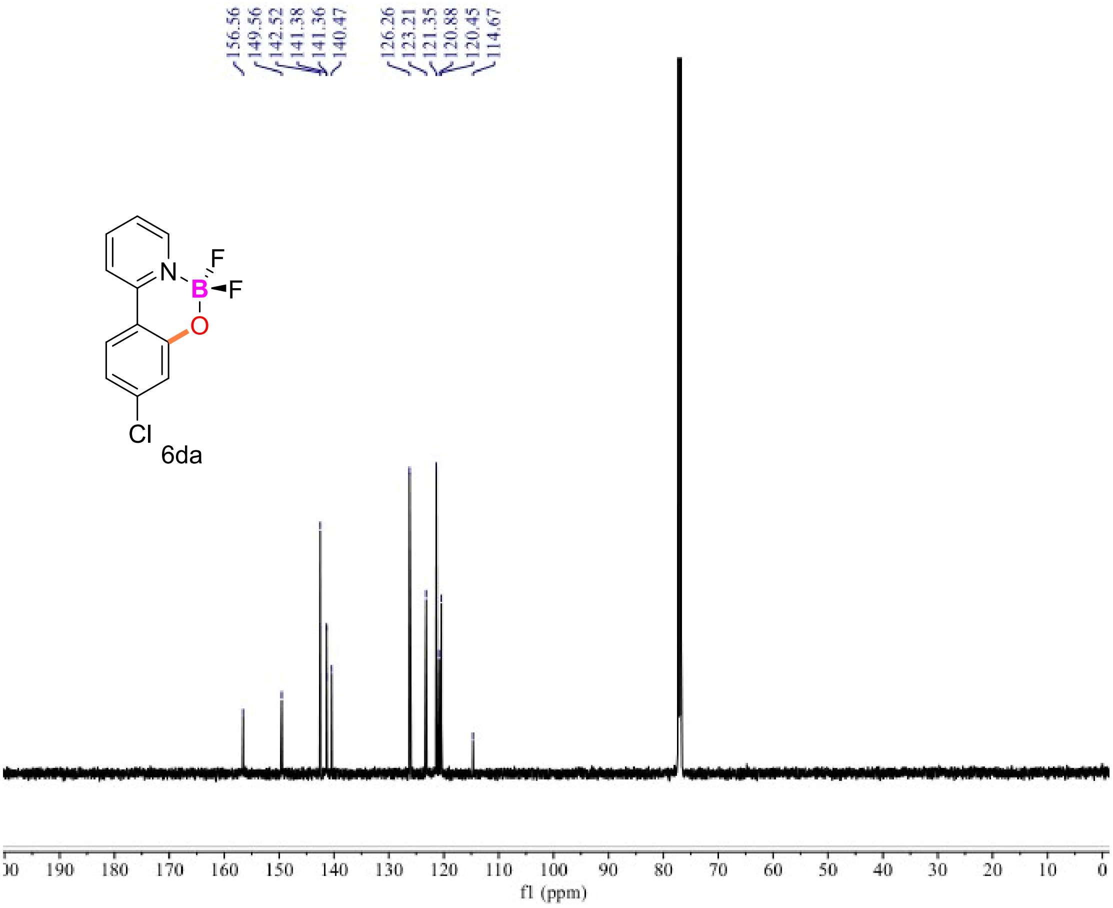
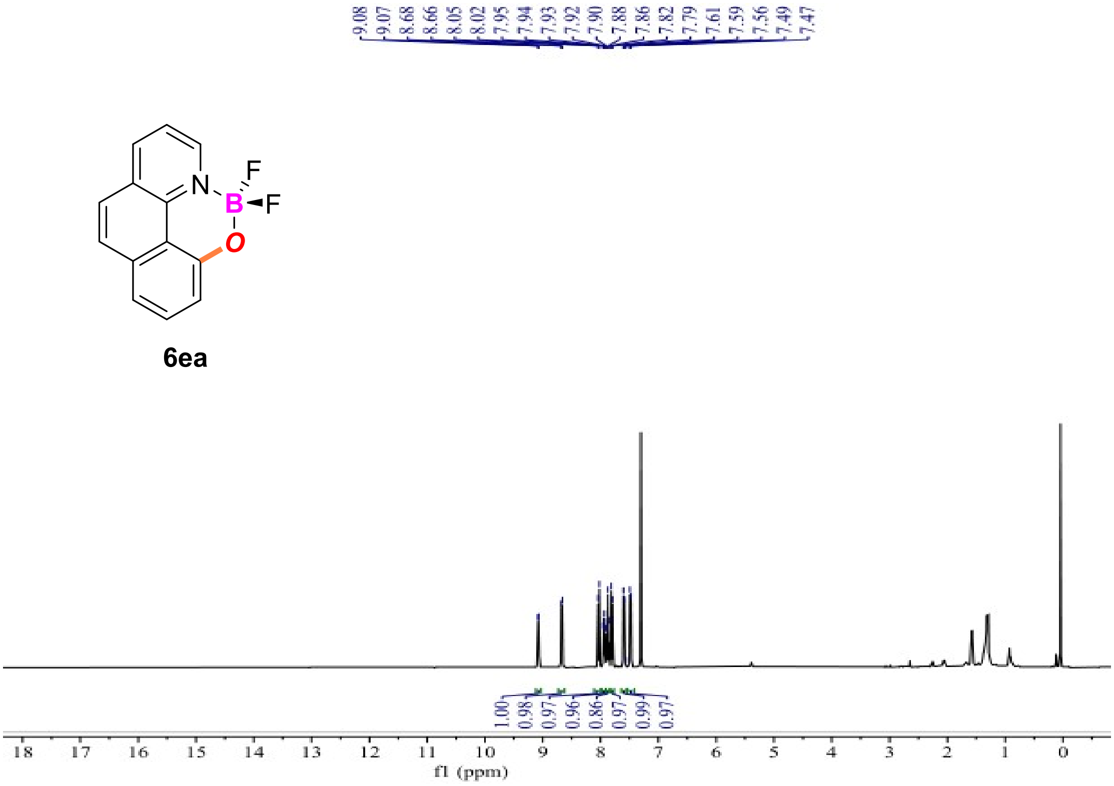
8.21
8.20
8.20
8.11
8.09
8.07
7.76
7.75
7.74
7.72
7.66
7.63
7.62
7.61
7.20
7.19
7.18
7.16
7.05
7.04
7.04
7.02
7.02
6.98
N
B
F
F
O
Cl
6da
1.00
0.94
1.04
0.99
0.99
0.83
0.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)



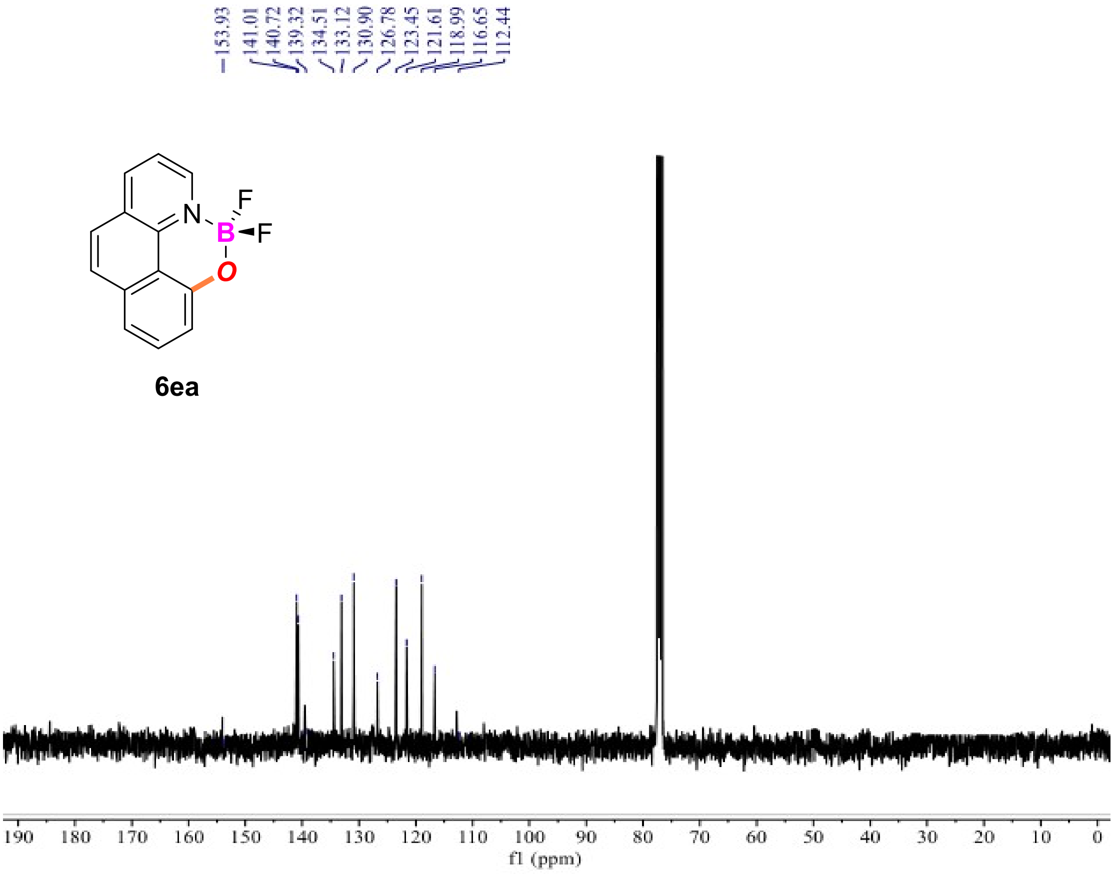
6da

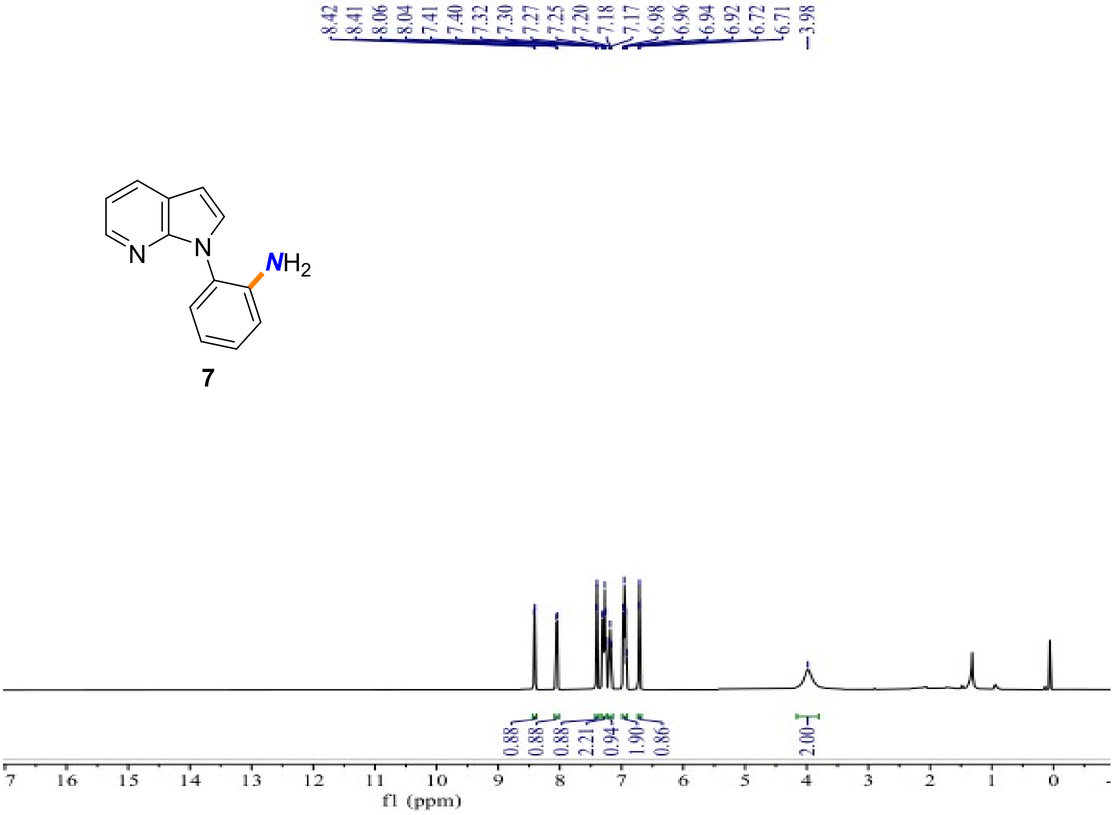
156.56
149.56
142.52
141.38
141.36
140.47
126.26
123.21
121.35
120.88
120.45
114.67
N
B
F
F
O
Cl
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



6ea

9.08
9.07
8.68
8.66
8.05
8.02
7.95
7.94
7.93
7.92
7.90
7.88
7.86
7.82
7.79
7.61
7.59
7.56
7.49
7.47
N
B
F
F
O
1.00
0.98
0.97
0.96
0.86
0.97
0.99
0.97
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


153.93
141.01
140.72
139.32
134.51
133.12
130.90
126.78
123.45
121.61
118.99
116.65
112.44
N
B
F
F
O
6ea
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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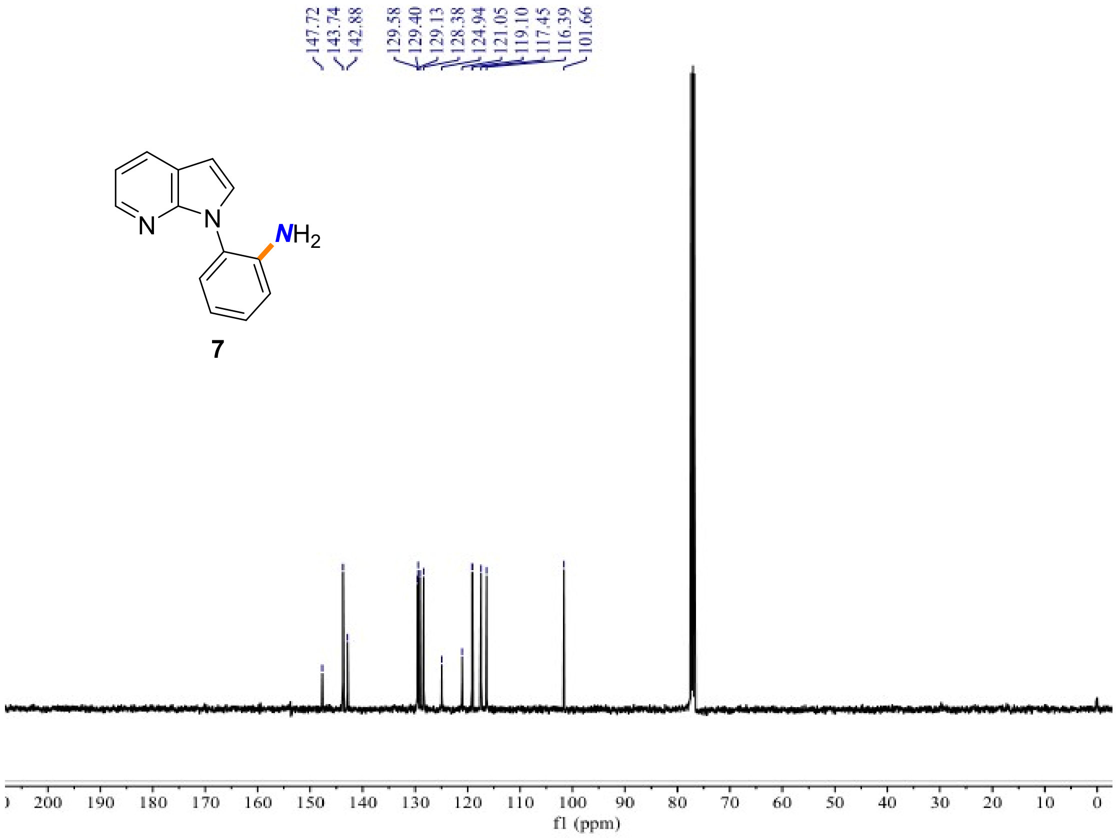
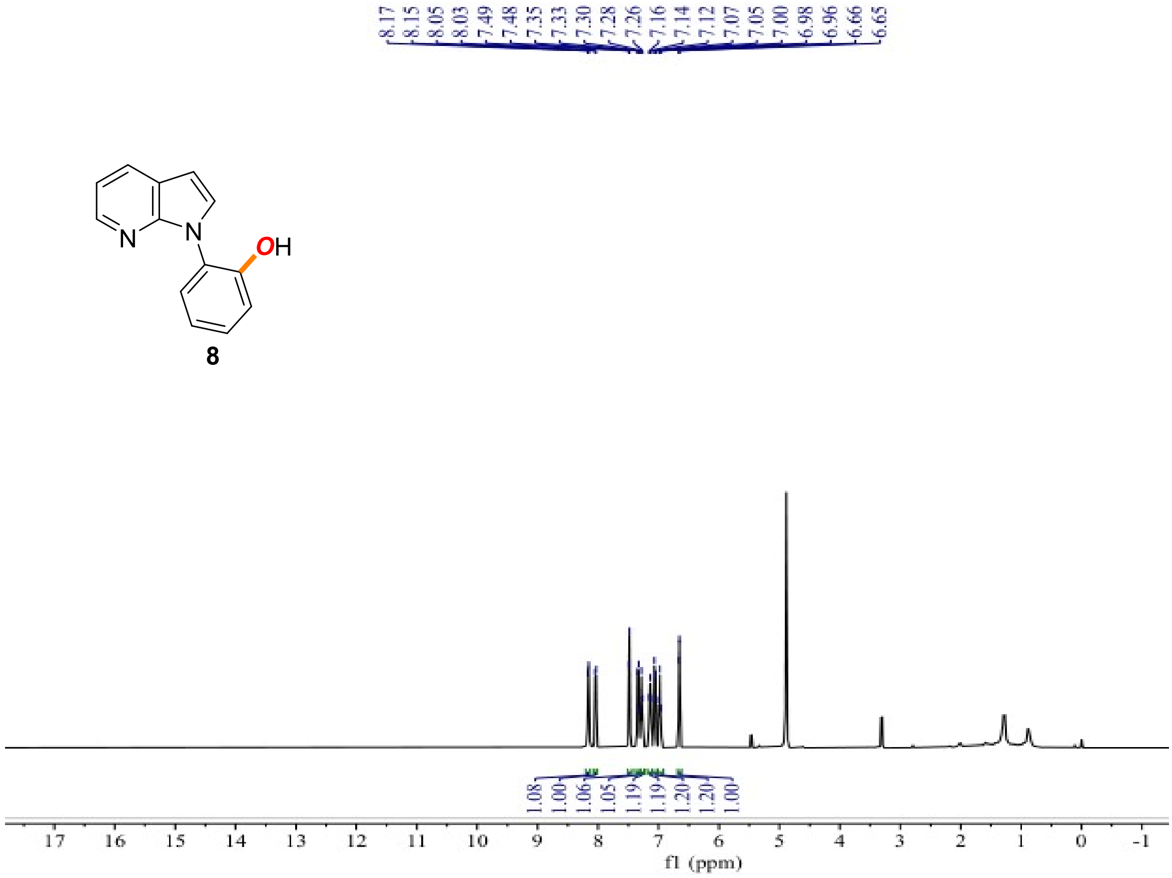
7.32
7.30
7.27
7.25
7.20
7.18
7.17
6.98
6.96
6.94
6.92
6.72
6.71
3.98
N
N
NH2
7
0.88
0.88
0.88
2.21
0.94
1.90
0.86
2.00
7 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


147.72
143.74
142.88
129.58
129.40
129.13
128.38
124.94
121.05
119.10
117.45
116.39
101.66
N
N
NH2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

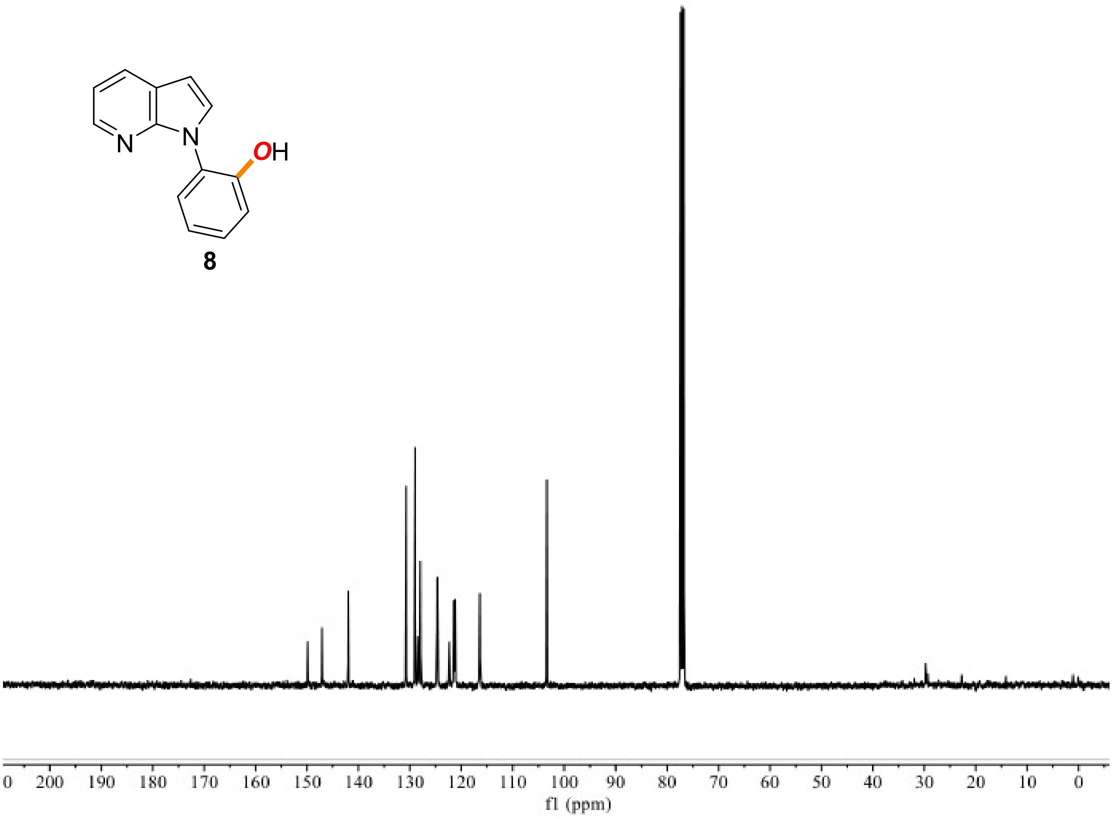
7

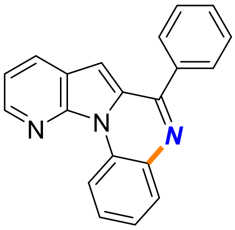

8.17
8.15
8.05
8.03
7.49
7.48
7.35
7.33
7.30
7.28
7.26
7.16
7.14
7.12
7.07
7.05
7.00
6.98
6.96
6.66
6.65
N
N
OH
1.08
1.00
1.06
1.05
1.19
1.19
1.20
1.20
1.00
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

8

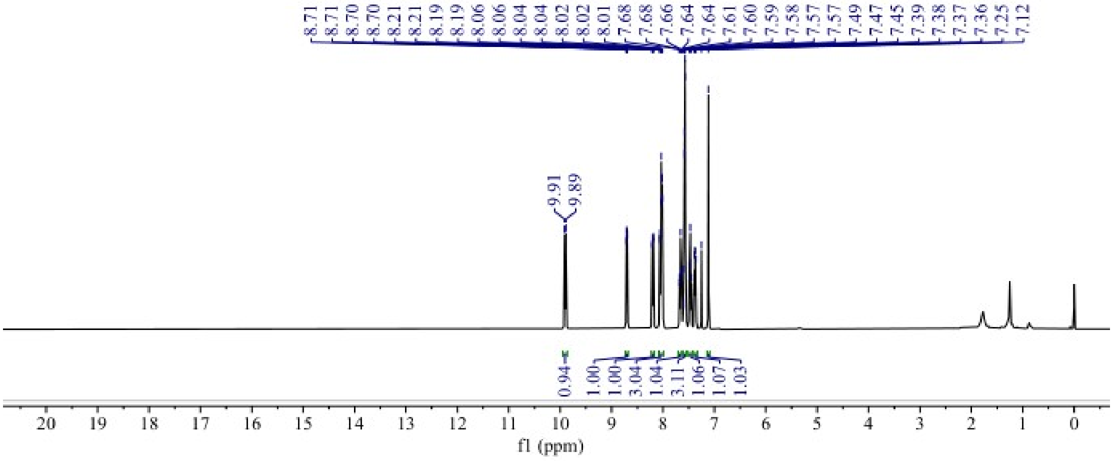
N
N
OH

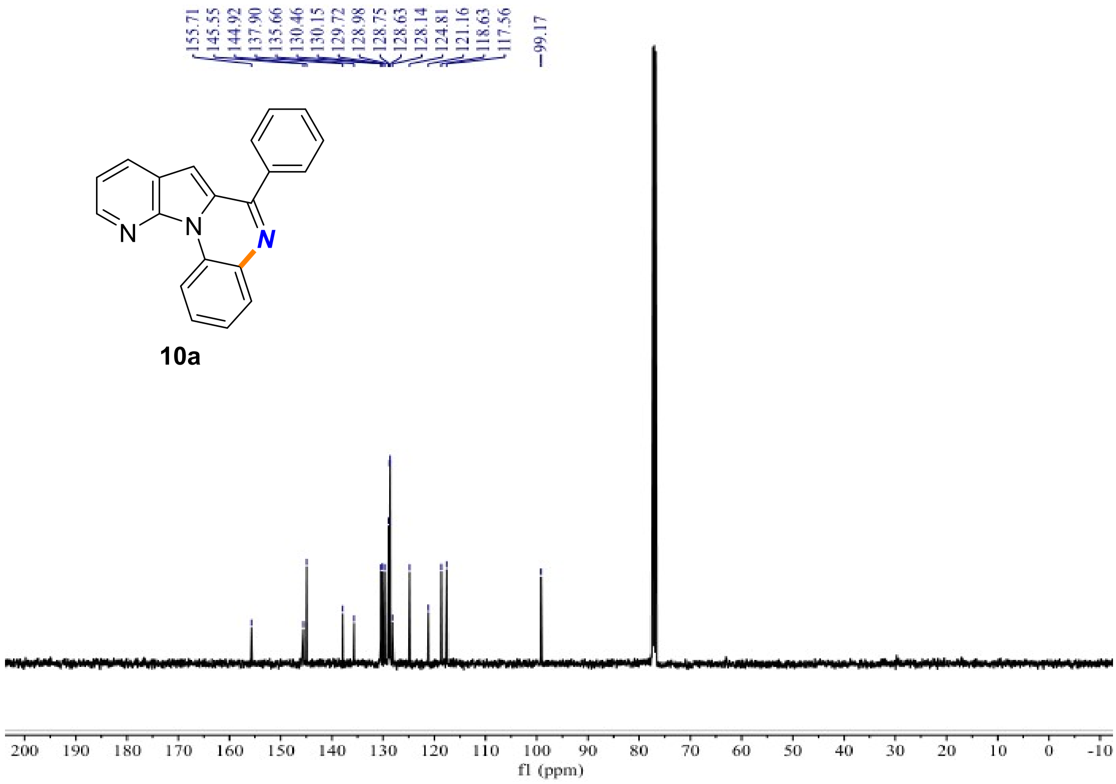
8


0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

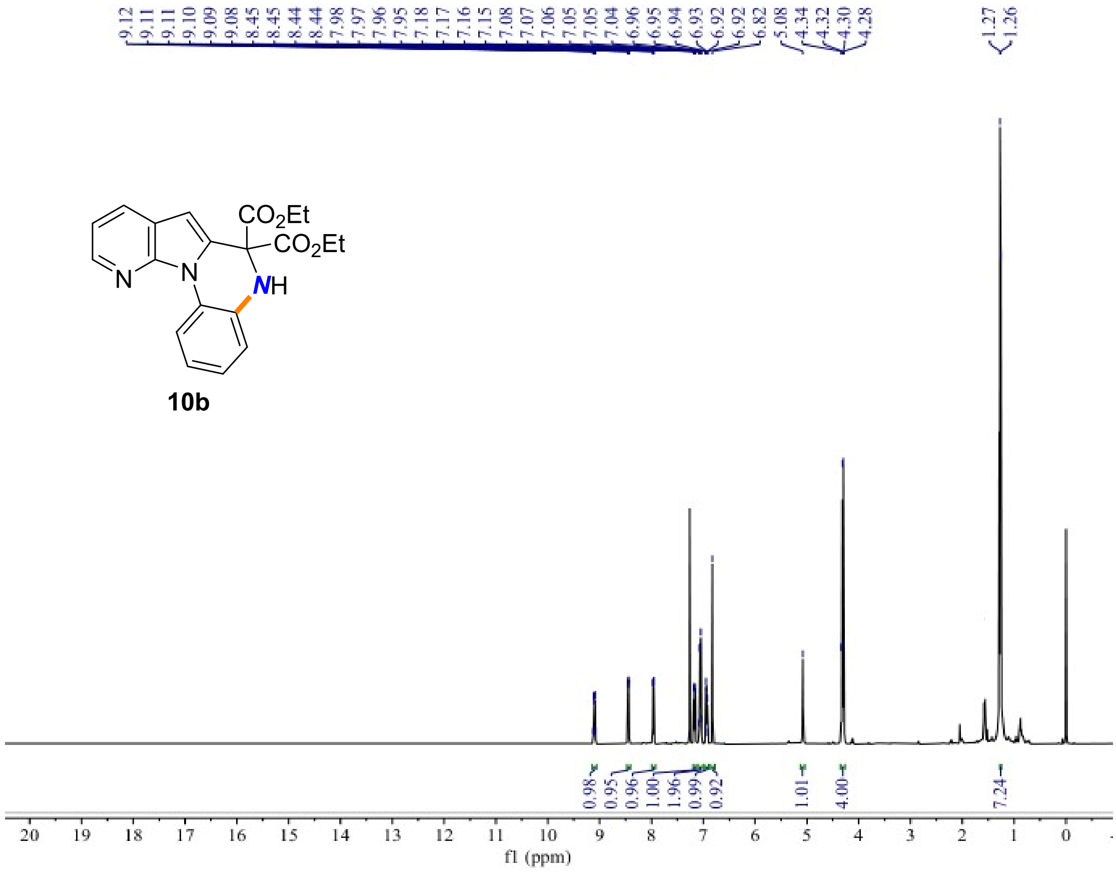

N
N
N

10a

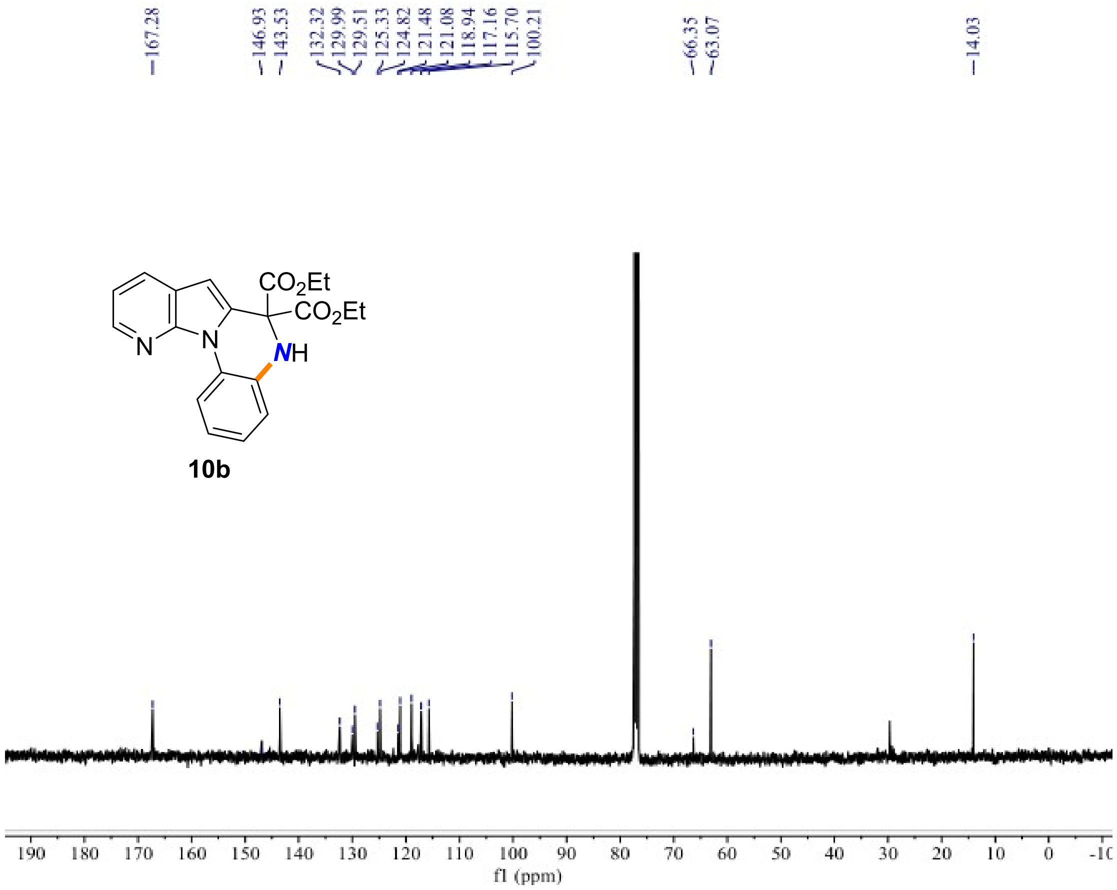

8.71
8.71
8.70
8.70
8.21
8.21
8.19
8.19
8.06
8.06
8.04
8.04
8.02
8.02
8.01
7.68
7.68
7.66
7.64
7.64
7.61
7.60
7.59
7.58
7.57
7.57
7.49
7.47
7.45
7.39
7.38
7.37
7.36
7.25
7.12
9.91
9.89
0.94
1.00
1.00
3.04
1.04
3.11
1.06
1.07
1.03
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


155.71
145.55
144.92
137.90
135.66
130.46
130.15
129.72
128.98
128.75
128.63
128.14
124.81
121.16
118.63
117.56
99.17
N
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10a


9.12
9.11
9.11
9.10
9.09
9.08
8.45
8.45
8.44
8.44
7.98
7.97
7.96
7.95
7.18
7.17
7.16
7.15
7.08
7.07
7.06
7.05
7.05
7.04
6.96
6.95
6.94
6.93
6.92
6.92
6.82
5.08
4.34
4.32
4.30
4.28
1.27
1.26
CO2Et
CO2Et
N
N
NH
0.98
0.95
0.96
1.00
1.96
0.99
0.92
1.01
4.00
7.24
20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

10b


167.28
146.93
143.53
132.32
129.99
129.51
125.33
124.82
121.48
121.08
118.94
117.16
115.70
100.21
66.35
63.07
14.03
CO2Et
CO2Et
N
N
NH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

10b