Supporting Information

Rhodium(III)-Catalyzed Switchable C−H Acylmethylation and Annulation of 2,2'-Bipyridine Derivatives with Sulfoxonium Ylides

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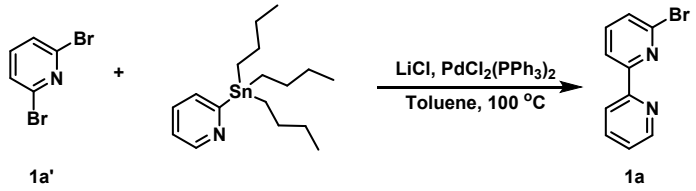
General information:

The ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates. Melting points were obtained on a Yanaco-241 apparatus and have been corrected with standards. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Preparation of Starting Materials:

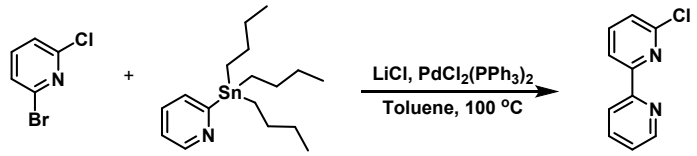
Synthesis of 1a[1]



1a' 1a

A toluene solution (35.0 mL) containing **1a'** (1.26 g, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (1.95 g, 5.3 mmol), LiCl (2.5 g, 53.0 mmol), and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were evaporated to dryness under reduced pressure. The obtained yellow solid was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

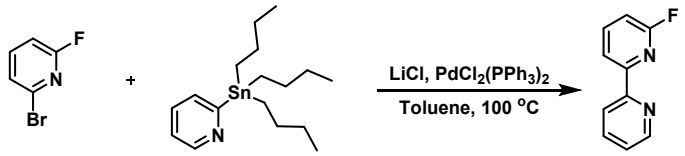
Synthesis of 1b[1]



1b' 1b

A toluene solution (35.0 mL) containing **1b'** (1.02 g, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.95 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol), and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were evaporated to dryness under reduced pressure. The obtained yellow solid was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

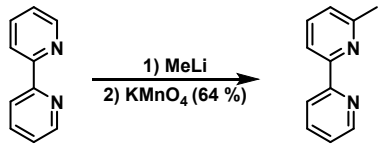
Synthesis of 1c[1]



1c' 1c

A toluene solution (35.0 mL) containing **1c'** (932.7 mg, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.95 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol), and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were evaporated to dryness under reduced pressure. The obtained white solid was dissolved in PE/EA (95:5, v/v), and purified on a silica gel column.

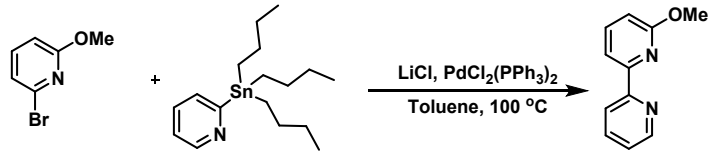
Synthesis of 1d[1]



1d

4.0 mL of 1.6 M methyllithium in diethyl ether (67.5 mmol) was added dropwise to 40.0 mL of a diethyl ether solution containing 2,2'-bi-pyridine (1.0 g, 6.4 mmol) at 0°C. After complete addition (approximately 1 h), the resulting brown solution was gently refluxed for 3 h under N_2. It was then allowed to cool to room temperature and water was added with stirring, resulting in a biphasic yellow solution. The aqueous layer was separated from the organic layer and extracted three times with diethyl ether. The combined organic layers were washed twice with brine followed by addition of anhydrous Na_2SO_4 to remove residual water. The solution was then decanted into a round-bottom flask and the ether was removed by rotary evaporation. The resulting orange oil was oxidized with approximately 100.0 mL of a saturated $KMnO_4$/acetone solution until formation of MnO_2 ceased. The MnO_2 was removed by vacuum filtration through celite. The filtrate was placed in a round-bottom flask and acetone was removed by rotary evaporation. The purification of the crude product by columnchromatography (heptane/EtOAc: 1/1) give the desired product **1d**.

Synthesis of 1e[1]

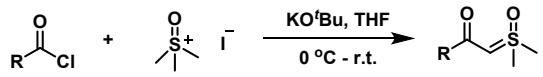


1e' 1e

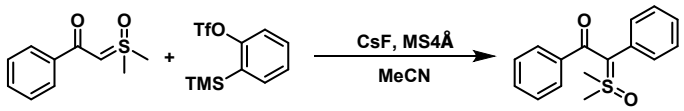
A toluene solution (35.0 mL) containing **1e'** (996.5 mg, 5.3 mmol), 2-(tri-n-butylstannyl)pyridine (2.9 g, 8.0 mmol), LiCl (2.5 g, 53.0 mmol), and $[PdCl_2(PPh_3)_2]$ (294.8 mg, 0.42 mmol) was deaerated by bubbling N_2 through it. The mixture was then refluxed under N_2 for 18 h, and an aqueous solution (10.0 mL) of NaF (2.2 g, 53.0 mmol) was added to the solution at room temperature. The resultant solution was further stirred at ambient temperature for 30 min. An insoluble solid was filtered off, and the filtrate was treated with a 5% Na_2CO_3 aqueous solution in a separating funnel. The organic layer was dried with anhydrous sodium sulfate, and the solvents were evaporated to dryness under reduced pressure. The obtained oil was dissolved in PE/EA (95:5, v/v), and purified on a silica gel

column.

Synthesis of 2

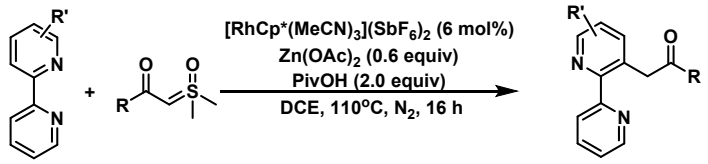


Ylides **2a-2q**[2] were prepared according to the reported procedures. To a stirred solution of potassium *tert*-butoxide (3.0 g, 27.2 mmol) in THF (30.0 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at room temperature. The resulting mixture is refluxed for 2 h. Then reaction mixture is cooled to 0 °C, followed by addition of acyl chlorides (7.0 mmol) in THF (5.0 mL). The reaction was allowed to room temperature and stirred for 3 h. Next, the solvent was evaporated and water (15.0 mL) and ethyl acetate (20.0 mL) were added to the resulting slurry. The layers were separated and the aqueous layer was washed with ethyl acetate (2 x 30 mL) and the organic layers were combined. The organic solutionwas dried over anhydrous sodium sulphate (Na_2SO_4), filtered over a sintered funnel, and evaporated to dryness. The crude product was purified by flash chromatography over silica gel using EtOAc/MeOH to afford the corresponding sulfoxonium ylides.



To a 3 mL glass vial containing a magnetic stirrer and fitted with a Teflon cap, the respective β-ketosulfoxonium ylide (1.0 equiv, 0.13 mmol), activated molecular sieves 4Å powder (25.0 mg), CsF (4.0 equiv, 77.4 mg, 0.51 mmol), and dry acetonitrile (1.0 mL) were added. Under vigorous stirring, the appropriate precursor of aryne (1.5 equiv, 0.19 mmol) was added in three portions (2.0 equiv in four portions for amino acid derivatives) at intervals of 1 hour (at 65 ºC). After 3 hours, the organic solvent was removed into rotary evaporator and the crude product purified by flash chromatography, employing the basic silica gel and mixtures of 0.5 to 2 % of MeOH in $CHCl_3$ to give the product **2r**[3].

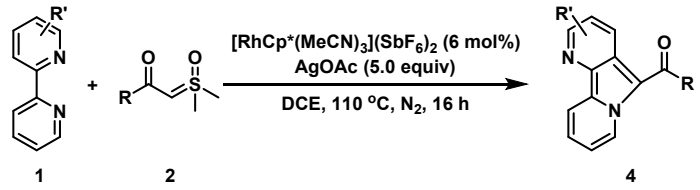
Synthesis of 3



A sealed tube contained **1** (0.2 mmol), **2** (0.4 mmol), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (10.0 mg, 0.012 mol), $Zn(OAc)_2$ (22.0 mg, 0.12 mmol) and PivOH (0.4 mmol, 2.0 equiv) was filled and

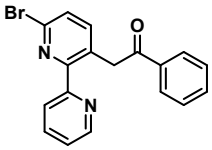
purged with nitrogen gas three times. Then DCE (4.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 16 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on silica gel to afford the desired pure product **3**.

Synthesis of 4



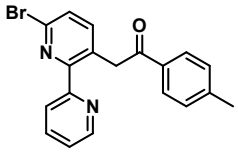
A sealed tube contained **1** (0.2 mmol), **2** (0.4 mmol), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (10.0 mg, 0.012 mol), and AgOAc (166.9 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (4.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 16 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on silica gel to afford the desired pure product **4**.

Characterization of Products:



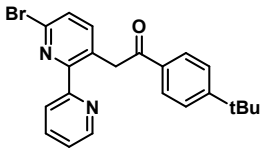
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-phenylethanone (**3aa**)

White solid (58 mg, 83%); M.P.: 122-124 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.19 (m, 1H), 8.10 – 8.07 (m, 1H), 8.01 – 7.98 (m, 2H), 7.78 – 7.72 (m, 1H), 7.61 – 7.56 (m, 1H), 7.53 – 7.47 (m, 4H), 7.16 – 7.12 (m, 1H), 4.73 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 156.2, 155.2, 147.5, 143.6, 139.6, 137.1, 136.9, 132.8, 129.2, 128.5, 128.1, 127.5, 123.9, 123.3, 43.3. **ESI-MS:** Calcd for $C_{18}H_{13}BrN_2O$: [M+H$^+$] 353.0284, found 353.0288.



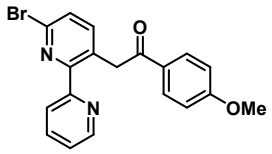
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(p-tolyl)ethanone (**3ab**)

White solid (60 mg, 82%); M.P.: 170-172 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 4.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.52 – 7.46 (m, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.12 (m, 1H), 4.71 (s, 2H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 156.3, 155.4, 147.6, 143.6, 143.5, 139.5, 136.8, 134.5, 129.4, 129.2, 128.3, 127.4, 124.0, 123.2, 43.1, 21.6. **ESI-MS:** Calcd for $C_{19}H_{15}BrN_2O$: [M+H$^+$] 367.0441, found 367.0447.



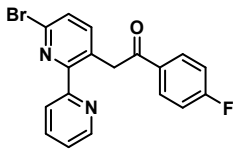
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(4-(*tert*-butyl)phenyl)ethanone (**3ac**)

White solid (69 mg, 85%); M.P.: 125-127 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 4.8, 0.8 Hz, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.79 – 7.73 (m, 1H), 7.50 – 7.46 (m, 4H), 7.19 – 7.14 (m, 1H), 4.74 (s, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 162.2, 157.6, 150.8, 147.3, 144.0, 137.6, 136.4, 132.4, 128.4, 128.1, 123.4, 122.6, 122.5, 110.5, 53.4, 53.3, 43.1. **ESI-MS:** Calcd for $C_{22}H_{21}BrN_2O$: [M+H$^+$] 409.0910, found 409.0919.



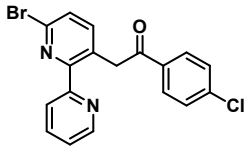
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(4-methoxyphenyl)ethanone (**3ad**)

White solid (61 mg, 80%); M.P.: 133-136 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.8 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.78 – 7.72 (m, 1H), 7.52 – 7.46 (m, 2H), 7.15 (dd, *J* = 7.6, 4.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.69 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3, 163.3, 156.4, 155.5, 147.6, 143.4, 136.8, 130.4, 130.0, 129.5, 127.4, 124.1, 123.2, 113.7, 55.4, 42.7. **ESI-MS:** Calcd for $C_{19}H_{15}BrN_2O_2$: [M+H$^+$] 383.0390, found 383.0396.



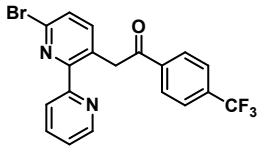
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(4-fluorophenyl)ethanone (**3ae**)

Gray solid (67 mg, 90%); M.P.: 137-139 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 4.4 Hz, 1H), 8.05 – 8.00 (m, 2H), 7.78 – 7.73 (m, 1H), 7.49 (s, 2H), 7.18 – 7.13 (m, 3H), 4.69 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 162.9, 160.6, 156.2, 152.3, 147.5, 146.4 (d, *J* = 7.0 Hz), 137.3, 136.8, 132.7, 128.5, 128.1, 123.7, 123.2, 109.0 (d, *J* = 39.0 Hz), 43.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -105.67. **ESI-MS:** Calcd for $C_{18}H_{12}BrFN_2O$: [M+H$^+$] 371.0190, found 371.0197.



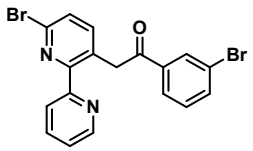
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(4-chlorophenyl)ethanone (**3af**)

White solid (66 mg, 86%); M.P.: 147-148 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 4.0 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.78 – 7.73 (m, 1H), 7.50 – 7.44 (m, 4H), 7.17 – 7.13 (m, 1H), 4.67 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 156.1, 155.0, 147.4, 143.6, 139.7, 139.1, 136.9, 135.5, 129.6, 128.9, 128.8, 127.5, 124.0, 123.4, 43.3. **ESI-MS:** Calcd for $C_{18}H_{12}BrClN_2O$: [M+H$^+$] 386.9894, found 386.9898.



2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (**3ag**)

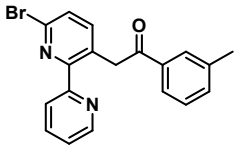
White solid (44 mg, 52%); M.P.: 161-163 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.98 – 7.95 (m, 1H), 7.79 – 7.73 (m, 3H), 7.51 (s, 2H), 7.16 – 7.12 (m, 1H), 4.70 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 155.9, 154.8, 147.2, 143.7, 140.1, 139.8, 137.0, 134.1 (q, *J* = 33.0 Hz), 128.7, 128.5, 127.6, 125.6, 124.0, 123.7 (q, *J* = 271.0 Hz), 123.4, 43.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.97. **ESI-MS:** Calcd for $C_{19}H_{12}BrF_3N_2O$: [M+H$^+$] 421.0158, found 421.0166.



2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(3-bromophenyl)ethanone (**3ah**)

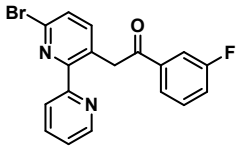
White solid (68 mg, 79%); M.P.: 152-154 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H), 8.05 (d, *J* = 4.8 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.78 – 7.69 (m, 2H),

7.49 (s, 2H), 7.40 – 7.35 (m, 1H), 7.17 – 7.13 (m, 1H), 4.66 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 155.9, 154.8, 147.3, 143.6, 139.7, 139.0, 136.9, 135.6, 131.2, 130.1, 128.7, 127.5, 126.6, 123.9, 123.4, 122.8, 43.4. **ESI-MS:** Calcd for $C_{18}H_{12}Br_2N_2O$: [M+H$^+$] 430.9389, found 430.9395.



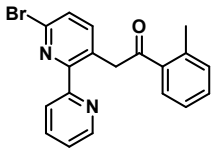
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(m-tolyl)ethanone (**3ai**)

White solid (55 mg, 75%); M.P.: 112-114 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.15 – 8.12 (m, 1H), 7.80 – 7.73 (m, 3H), 7.52 – 7.46 (m, 2H), 7.41 – 7.34 (m, 2H), 7.17 – 7.13 (m, 1H), 4.71 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.8, 156.3, 155.4, 147.5, 143.5, 139.5, 138.3, 137.1, 136.8, 133.6, 129.3, 128.7, 128.4, 127.4, 125.4, 124.0, 123.2, 43.3, 21.3. **ESI-MS:** Calcd for $C_{19}H_{15}BrN_2O$: [M+H$^+$] 367.0441, found 367.0450.



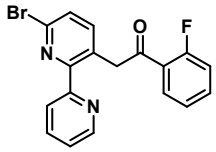
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(3-fluorophenyl)ethanone (**3aj**)

White solid (52 mg, 70%); M.P.: 130-132 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 4.4 Hz, 1H), 7.76 (dd, *J* = 18.8, 7.8 Hz, 2H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.32 – 7.26 (m, 1H), 7.16 – 7.12 (m, 1H), 4.67 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3, 164.1, 161.6, 156.1, 155.0, 147.4, 143.6, 139.7, 139.4 (d, *J* = 6.0 Hz), 136.9, 130.2 (d, *J* = 7.0 Hz), 128.8, 127.5, 123.8 (d, *J* = 3.0 Hz), 123.4, 119.7 (d, *J* = 22.0 Hz), 114.9 (d, *J* = 23.0 Hz), 43.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.88. **ESI-MS:** Calcd for $C_{18}H_{12}BrFN_2O$: [M+H$^+$] 371.0190, found 371.0196.



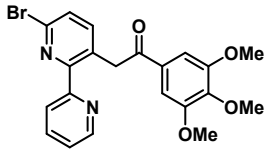
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(o-tolyl)ethan-1-one (**3ak**)

White solid (45 mg, 61%); M.P.: 120-121 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 1H), 8.11 – 8.09 (m, 1H), 7.75 – 7.68 (m, 2H), 7.49 – 7.43 (m, 2H), 7.38 – 7.33 (m, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.09 (m, 1H), 4.59 (s, 2H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 156.4, 155.4, 147.4, 143.6, 139.5, 138.5, 137.9, 136.8, 131.9, 131.1, 129.4, 128.3, 127.4, 125.5, 124.1, 123.2, 46.1, 21.1. **ESI-MS:** Calcd for $C_{19}H_{15}BrN_2O$: [M+H$^+$] 367.0441, found 367.0443.



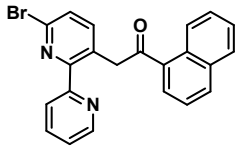
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(2-fluorophenyl)ethan-1-one (**3al**)

Yellow oil (53 mg, 71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.85 – 7.80 (m, 1H), 7.76 – 7.71 (m, 1H), 7.55 – 7.47 (m, 3H), 7.28 – 7.23 (m, 1H), 7.19 – 7.10 (m, 2H), 4.63 (d, *J* = 2.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9, 162.7, 160.2, 156.0, 155.1, 147.2, 143.7, 139.5, 136.7, 134.0 (d, *J* = 9.0 Hz), 130.9 (d, *J* = 3.0 Hz), 129.0, 127.4, 126.2 (d, *J* = 13.0 Hz), 123.8, 123.2, 116.5 (d, *J* = 24.0 Hz), 48.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.76. **ESI-MS:** Calcd for $C_{18}H_{12}BrFN_2O$: [M+H$^+$] 371.0190, found 371.0186.



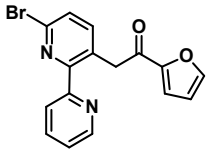
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(3,4,5-trimethoxyphenyl)ethanone (**3am**)

White solid (52 mg, 59%); M.P.: 157-159 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 4.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.50 – 7.45 (m, 2H), 7.27 (s, 2H), 7.20 – 7.16 (m, 1H), 4.72 (s, 2H), 3.92 (s, 3H), 3.87 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 156.4, 155.1, 153.0, 147.5, 143.2, 142.4, 139.5, 136.9, 132.2, 129.2, 127.5, 124.1, 123.3, 105.8, 60.8, 56.3, 42.9. **ESI-MS:** Calcd for $C_{21}H_{19}BrN_2O_4$: [M+H$^+$] 443.0601, found 443.0604.



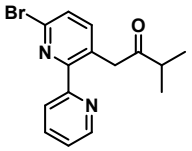
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(naphthalen-1-yl)ethanone (**3an**)

Colorless oil (64 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 – 8.45 (m, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.90 – 7.88 (m, 2H), 7.75 – 7.69 (m, 1H), 7.58 – 7.49 (m, 5H), 7.07 – 7.03 (m, 1H), 4.77 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.6, 156.3, 155.5, 147.6, 143.7, 139.6, 136.8, 136.1, 133.9, 132.4, 130.2, 129.2, 128.2, 127.6, 127.5, 127.0, 126.4, 126.1, 124.2, 124.0, 123.2, 46.7. **ESI-MS:** Calcd for $C_{22}H_{15}BrN_2O$: [M+H$^+$] 403.0441, found 403.0448.



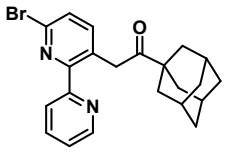
2-(6-bromo-[2,2'-bipyridin]-3-yl)-1-(furan-2-yl)ethanone (**3ao**)

Gray solid (51 mg, 74%); M.P.: 112-114 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.59 – 7.57 (m, 1H), 7.50 (dd, *J* = 20.0, 8.0 Hz, 2H), 7.21 – 7.16 (m, 2H), 6.55 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.56 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.6, 156.2, 155.5, 152.6, 147.5, 146.0, 143.5, 139.6, 136.8, 128.3, 127.4, 124.0, 123.3, 116.7, 112.2, 42.8. **ESI-MS:** Calcd for $C_{16}H_{11}BrN_2O_2$: [M+H$^+$] 343.0077, found 343.0078.



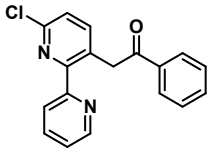
1-(6-bromo-[2,2'-bipyridin]-3-yl)-3-methylbutan-2-one (**3ap**)

White solid (32 mg, 50%); M.P.: 120-122 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.8 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.44 (dd, *J* = 20.8, 8.0 Hz, 2H), 7.30 – 7.27 (m, 1H), 4.21 (s, 2H), 2.84 – 2.77 (m, 1H), 1.11 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.3, 156.7, 155.7, 147.5, 143.3, 139.4, 136.9, 129.0, 127.4, 124.3, 123.3, 45.0, 40.6, 18.2. **ESI-MS:** Calcd for $C_{15}H_{15}BrN_2O$: [M+H$^+$] 319.0441, found 319.0448.



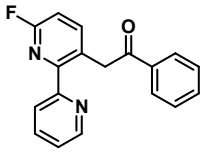
1-((1s,3s)-adamantan-1-yl)-2-(6-bromo-[2,2'-bipyridin]-3-yl)ethan-1-one (**3aq**)

White solid (63 mg, 77%); M.P.: 129-131 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 – 8.53 (m, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.23 (m, 1H), 4.31 (s, 2H), 2.03 (s, 3H), 1.81 (d, *J* = 2.8 Hz, 6H), 1.71 (dd, *J* = 27.6, 12.0 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 211.5, 157.1, 156.2, 147.7, 143.2, 139.2, 136.8, 129.4, 127.2, 124.5, 123.1, 46.5, 40.8, 38.5, 36.5, 28.0. **ESI-MS:** Calcd for $C_{22}H_{23}BrN_2O$: [M+H$^+$] 410.0994, found 410.1001.



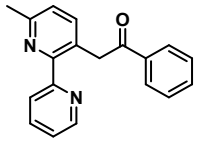
2-(6-chloro-[2,2'-bipyridin]-3-yl)-1-phenylethan-1-one (**3ba**)

White solid (54 mg, 88%); M.P.: 101-102 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 8.09 (dd, *J* = 4.8, 0.8 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.78 – 7.72 (m, 1H), 7.63 – 7.56 (m, 2H), 7.51 – 7.46 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.12 (m, 1H), 4.74 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 156.3, 154.7, 149.1, 147.5, 143.9, 137.2, 136.9, 132.8, 128.8, 128.5, 128.1, 123.9, 123.7, 123.2, 43.2. **ESI-MS:** Calcd for $C_{18}H_{13}ClN_2O$: [M+H$^+$] 309.0789, found 309.0798.



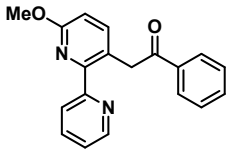
2-(6-fluoro-[2,2'-bipyridin]-3-yl)-1-phenylethan-1-one (**3ca**)

White solid (50 mg, 85%); M.P.: 129-131 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 4.4 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.78 – 7.72 (m, 2H), 7.62 – 7.57 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.11 (m, 1H), 6.97 (dd, *J* = 8.0, 3.6 Hz, 1H), 4.76 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 166.8, 164.3, 156.2, 155.1, 147.4, 143.6, 139.7, 136.9, 133.6 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.0 Hz), 129.0, 127.5, 124.0, 115.6 (d, *J* = 21.0 Hz), 43.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.17. **ESI-MS:** Calcd for $C_{18}H_{13}FN_2O$: [M+H$^+$] 293.1085, found 293.1094.



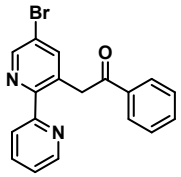
2-(6-methyl-[2,2'-bipyridin]-3-yl)-1-phenylethan-1-one (**3da**)

Colorless oil (48 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 – 8.16 (m, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.98 – 7.95 (m, 2H), 7.77 – 7.71 (m, 1H), 7.58 – 7.53 (m, 2H), 7.48 – 7.43 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.10 (m, 1H), 4.67 (s, 2H), 2.63 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.4, 158.2, 156.5, 154.3, 147.6, 141.0, 137.3, 136.7, 132.7, 128.5, 128.2, 126.5, 123.9, 122.9, 122.6, 43.2, 24.3. **ESI-MS:** Calcd for $C_{19}H_{16}N_2O$: [M+H$^+$] 289.1335, found 289.1335.



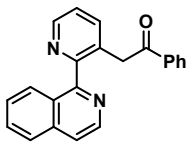
2-(6-methoxy-[2,2'-bipyridin]-3-yl)-1-phenylethan-1-one (**3ea**)

White solid (50 mg, 82%); M.P.: 128-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 4.4 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.76 – 7.70 (m, 1H), 7.59 – 7.52 (m, 2H), 7.50 – 7.45 (m, 2H), 7.12 – 7.08 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 4.71 (s, 2H), 4.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 162.2, 157.6, 150.8, 147.3, 144.0, 137.6, 136.4, 132.4, 128.4, 128.1, 123.4, 122.6, 122.5, 110.5, 53.3, 43.1. **ESI-MS:** Calcd for $C_{19}H_{16}N_2O_2$: [M+H$^+$] 305.1285, found 305.1283.



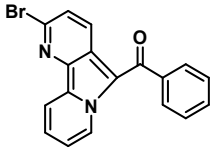
2-(5-bromo-[2,2'-bipyridin]-3-yl)-1-phenylethan-1-one (**3fa**)

White solid (18 mg, 25%); M.P.: 102-103 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.08 – 8.06 (m, 1H), 8.01 – 7.98 (m, 2H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.62 – 7.57 (m, 1H), 7.52 – 7.47 (m, 2H), 7.16 – 7.11 (m, 1H), 4.72 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 157.0, 153.2, 148.7, 147.5, 143.2, 137.2, 136.8, 132.8, 131.8, 128.6, 128.2, 123.6, 123.0, 120.2, 43.7. **ESI-MS:** Calcd for $C_{18}H_{13}BrN_2O$: [M+H$^+$] 353.0284, found 353.0290.



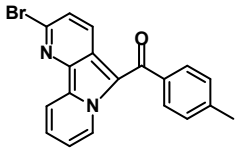
2-(2-(isoquinolin-1-yl)pyridin-3-yl)-1-phenylethan-1-one (**3ga**)

Colorless oil (34 mg, 52%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.36 (d, *J* = 6.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.64 – 7.55 (m, 4H), 7.49 – 7.45 (m, 1H), 7.43 – 7.35 (m, 2H), 7.25 – 7.20 (m, 2H), 4.32 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 158.1, 156.6, 147.5, 141.3, 139.7, 136.9, 136.4, 133.0, 130.6, 130.3, 128.4, 128.1, 127.6, 127.4, 127.3, 126.7, 123.3, 120.9, 41.9. **ESI-MS:** Calcd for $C_{22}H_{16}N_2O$: [M+H$^+$] 325.1335, found 325.1339.



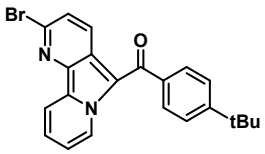
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4aa**)

Yellow solid (52 mg, 73%); M.P.: 129-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.50 (d, *J* = 6.8 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.27 – 7.24 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.5, 141.5, 136.5, 135.7, 132.9, 130.8, 129.4, 128.8, 128.7, 128.1, 126.9, 126.0, 124.2, 120.1, 118.1, 111.4. **ESI-MS:** Calcd for $C_{18}H_{11}BrN_2O$: [M+H$^+$] 351.0128, found 351.0128.



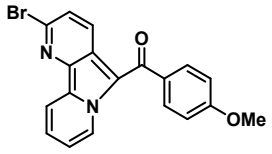
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(p-tolyl)methanone (**4ab**)

Yellow solid (51 mg, 70%); M.P.: 166-169 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (d, *J* = 7.2 Hz, 1H), 8.56 – 8.53 (m, 1H), 7.62 – 7.56 (m, 3H), 7.48 – 7.44 (m, 1H), 7.33 – 7.27 (m, 3H), 7.12 (d, *J* = 8.8 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 141.3, 138.7, 136.4, 135.7, 132.8, 129.7, 129.3, 128.7, 128.4, 126.8, 125.7, 124.2, 119.9, 118.1, 111.6, 21.6. **ESI-MS:** Calcd for $C_{19}H_{13}BrN_2O$: [M+H$^+$] 365.0284, found 365.0285.



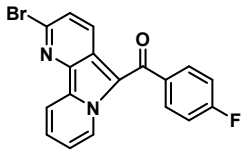
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(4-(*tert*-butyl)phenyl)methanone (**4ac**)

Yellow solid (61 mg, 75%); M.P.: 178-179 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (d, *J* = 6.8 Hz, 1H), 8.55 (d, *J* = 8.8 Hz, 1H), 7.63 – 7.57 (m, 3H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 1.40 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.7, 154.5, 138.6, 136.4, 135.6, 132.7, 129.6, 128.7, 128.2, 126.8, 125.7, 125.5, 124.1, 119.9, 118.1, 111.6, 35.0, 31.24. **ESI-MS:** Calcd for $C_{22}H_{19}BrN_2O$: [M+H$^+$] 407.0754, found 407.0759.



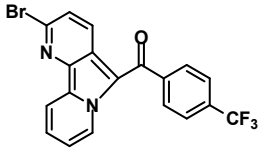
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(4-methoxyphenyl)methanone (**4ad**)

Yellow solid (55 mg, 73%); M.P.: 218-219 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.42 (d, *J* = 7.2 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.34 – 7.26 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 162.0, 136.3, 135.5, 133.8, 132.5, 130.6, 129.6, 128.6, 126.7, 125.4, 123.9, 119.8, 118.1, 113.9, 111.6, 55.5. **ESI-MS:** Calcd for $C_{19}H_{13}BrN_2O_2$: [M+H$^+$] 381.0233, found 381.0236.



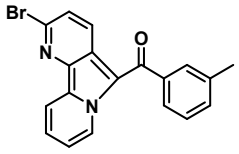
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(4-fluorophenyl)methanone (**4ae**)

Yellow solid (56 mg, 77%); M.P.: 184-187 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.52 (d, *J* = 7.2 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.73 – 7.67 (m, 1H), 7.57 – 7.53 (m, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.1, 165.5, 163.0, 137.6, 136.5, 135.7, 133.0, 130.6 (d, *J* = 8.0 Hz) 129.0 (d, *J* = 36.0 Hz), 127.0, 126.1, 124.0, 120.1, 118.1, 115.8 (d, *J* = 22.0 Hz), 111.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.42. **ESI-MS:** Calcd for $C_{18}H_{10}BrFN_2O$: [M+H$^+$] 369.0033, found 369.0036.



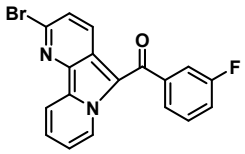
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(4-(trifluoromethyl)phenyl)methanone (**4ag**)

Yellow solid (33 mg, 40%); M.P.: 190-192 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.55 – 10.51 (m, 1H), 8.57 – 8.54 (m, 1H), 7.82 – 7.76 (m, 4H), 7.70 – 7.64 (m, 1H), 7.53 – 7.49 (m, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 9.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.5, 144.8, 136.8, 136.2, 133.6, 132.5 (q, *J* = 33.0 Hz), 129.1, 128.9, 128.5, 127.4, 126.9, 125.8, 123.8 (q, *J* = 271.0 Hz), 124.2, 120.5, 118.2, 111.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.65. **ESI-MS:** Calcd for $C_{19}H_{10}BrF_3N_2O$: [M+H$^+$] 419.0001, found 419.0001.



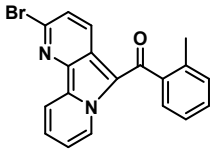
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(4-methoxyphenyl)methanone (**4ai**)

Yellow solid (51 mg, 70%); M.P.: 175-176 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.52 (d, *J* = 7.2 Hz, 1H), 8.58 – 8.54 (m, 1H), 7.65 – 7.60 (m, 1H), 7.51 – 7.40 (m, 5H), 7.31 – 7.27 (m, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.8, 141.6, 138.6, 136.5, 135.7, 132.9, 131.5, 129.6, 128.9, 128.6, 128.5, 126.9, 125.9, 125.2, 124.3, 120.1, 118.1, 111.5, 21.4. **ESI-MS:** Calcd for $C_{19}H_{13}BrN_2O$: [M+H$^+$] 365.0284, found 365.0292.



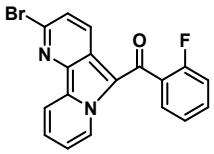
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(3-fluorophenyl)methanone (**4aj**)

Yellow solid (48 mg, 66%); M.P.: 208-210 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.51 (d, *J* = 7.2 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.54 – 7.47 (m, 2H), 7.44 – 7.41 (m, 1H), 7.39 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6 (d, *J* = 2.0 Hz), 164.0, 161.5, 143.7, 143.6, 136.7, 136.0, 130.5 (d, *J* = 8.0 Hz), 129.1 (d, *J* = 5.0 Hz), 127.2, 126.5, 124.3, 123.8 (d, *J* = 3.0 Hz), 120.3, 118.2, 117.7 (d, *J* = 21.0 Hz), 115.2 (d, *J* = 22.0 Hz), 111.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.38. **ESI-MS:** Calcd for $C_{18}H_{10}BrFN_2O$: [M+H$^+$] 369.0033, found 369.0038.



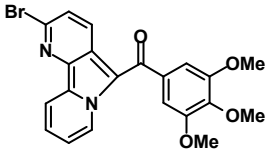
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(o-tolyl)methanone (**4ak**)

Yellow solid (56 mg, 76%); M.P.: 220-222 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.72 (d, *J* = 6.8 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.54 – 7.51 (m, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.31 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.45 (d, *J* = 8.8 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.0, 141.4, 136.6, 136.1, 134.8, 133.3, 130.9, 129.5, 129.2, 128.9, 127.5, 126.8, 126.5, 126.2, 124.5, 120.3, 118.1, 111.7, 19.0. **ESI-MS:** Calcd for $C_{19}H_{13}BrN_2O$: [M+H$^+$] 364.0211, found 364.0218.



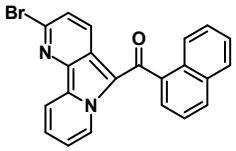
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(2-fluorophenyl)methanone (**4al**)

Yellow solid (67 mg, 91%); M.P.: 215-216 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.70 (d, *J* = 6.8 Hz, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.69 (m, 1H), 7.61 – 7.53 (m, 3H), 7.39 – 7.28 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 160.3, 157.9, 136.8, 136.4, 133.6, 131.8 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 17.0 Hz), 129.4 (d, *J* = 3.0 Hz), 128.6, 127.6, 127.0, 124.6 (d, *J* = 39.0 Hz), 120.5, 118.2, 116.6, 116.4 (d, *J* = 21.0 Hz), 112.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.96. **ESI-MS:** Calcd for $C_{18}H_{10}BrFN_2O$: [M+H$^+$] 367.9961, found 367.9966.



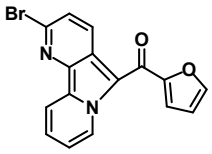
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(3,4,5-trimethoxyphenyl)methanone (**4am**)

Yellow solid (53 mg, 60%); M.P.: 221-222 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.47 – 10.44 (m, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.51 – 7.46 (m, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.93 (s, 2H), 3.96 (s, 3H), 3.84 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.8, 153.4, 140.3, 136.7, 136.6, 135.8, 133.1, 129.7, 128.8, 126.9, 126.0, 124.2, 120.1, 118.2, 111.2, 105.5, 61.0, 56.2. **ESI-MS:** Calcd for $C_{21}H_{17}BrN_2O_4$: [M+H$^+$] 441.0444, found 441.0447.



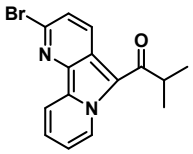
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(naphthalen-1-yl)methanone (**4an**)

Yellow solid (69 mg, 86%); M.P.: 222-224 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.81 (d, *J* = 7.2 Hz, 1H), 8.57 – 8.52 (m, 1H), 8.04 – 8.00 (m, 1H), 7.95 – 7.92 (m, 2H), 7.67 – 7.62 (m, 1H), 7.60 – 7.47 (m, 4H), 7.42 – 7.37 (m, 1H), 7.03 (dd, *J* = 8.8, 4.4 Hz, 1H), 6.25 (dd, *J* = 8.8, 0.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.0, 139.1, 136.5, 136.1, 133.6, 133.3, 130.2, 129.8, 129.3, 129.0, 128.2, 127.2, 126.9, 126.6, 126.4, 125.2, 125.1, 125.0, 124.3, 120.4, 118.0, 112.2. **ESI-MS:** Calcd for $C_{22}H_{13}BrN_2O$: [M+H$^+$] 401.0284, found 401.0293.



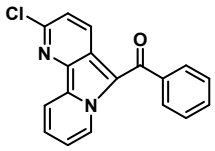
(2-bromopyrido[2,3-*a*]indolizin-5-yl)(furan-2-yl)methanone (**4ao**)

Yellow solid (56 mg, 82%); M.P.: 197-199 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.31 (d, *J* = 7.2 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.68 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.49 – 7.41 (m, 2H), 7.20 – 7.18 (m, 1H), 6.68 – 6.66 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 153.2, 144.8, 136.6, 135.8, 133.0, 129.7, 128.6, 127.0, 125.8, 123.4, 119.9, 118.2, 116.3, 112.2, 111.6. **ESI-MS:** Calcd for $C_{16}H_9BrN_2O_2$: [M+H$^+$] 340.9920, found 340.9927.



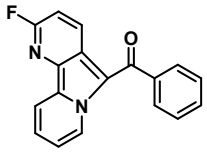
1-(2-bromopyrido[2,3-*a*]indolizin-5-yl)-2-methylpropan-1-one (**4ap**)

Yellow solid (41 mg, 64%); M.P.: 127-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.67 (d, *J* = 7.2 Hz, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.44 – 7.39 (m, 1H), 3.59 – 3.51 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.2, 135.9, 135.8, 132.5, 129.2, 129.0, 127.4, 125.4, 122.1, 120.1, 118.0, 110.9, 37.5, 19.2. **ESI-MS:** Calcd for $C_{15}H_{13}BrN_2O$: [M+H$^+$] 317.0284, found 317.0284.



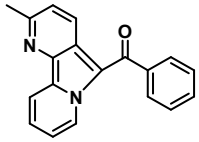
(2-chloropyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4ba**)

Yellow solid (49 mg, 80%); M.P.: 156-158 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.50 (d, *J* = 6.8 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 7.66 – 7.56 (m, 4H), 7.54 – 7.50 (m, 2H), 7.48 – 7.43 (m, 1H), 7.10 (dd, *J* = 24.8, 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.4, 146.0, 141.5, 134.9, 132.9, 130.7, 129.8, 128.8, 128.7, 128.1, 125.9, 124.0, 123.6, 120.0, 118.0, 111.4. **ESI-MS:** Calcd for $C_{18}H_{11}ClN_2O$: [M+H$^+$] 307.0633, found 307.0642.



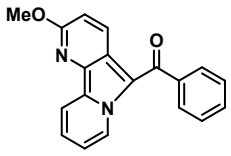
(2-fluoropyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4ca**)

Yellow solid (41 mg, 70%); M.P.: 139-142 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 7.2 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.66 – 7.57 (m, 4H), 7.53 – 7.48 (m, 1H), 7.32 – 7.27 (m, 1H), 6.92 (dd, *J* = 9.2, 1.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.1, 165.5, 163.0, 137.6, 136.5, 135.7, 133.0, 130.6 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 36.0 Hz), 127.0, 126.1, 124.0, 120.1, 118.1, 115.8 (d, *J* = 22.0 Hz), 111.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -70.16. **ESI-MS:** Calcd for $C_{18}H_{11}FN_2O$: [M+H$^+$] 291.0928, found 291.0932.



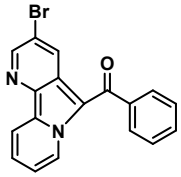
(2-methylpyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4da**)

Yellow solid (44 mg, 77%); M.P.: 173-175 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 7.2 Hz, 1H), 8.59 – 8.55 (m, 1H), 7.68 – 7.65 (m, 2H), 7.60 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 7.08 – 7.01 (m, 2H), 2.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.1, 154.3, 142.1, 135.8, 134.0, 130.4, 129.0, 128.6, 128.1, 127.4, 125.5, 124.2, 123.7, 119.5, 117.8, 111.5, 24.6. **ESI-MS:** Calcd for $C_{19}H_{14}N_2O$: [M+H$^+$] 287.1179, found 287.1186.



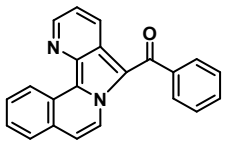
(2-methoxypyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4ea**)

Yellow solid (42 mg, 70%); **M.P.**: 189-190 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.47 (d, *J* = 7.2 Hz, 1H), 8.37 (d, *J* = 8.8 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.59 – 7.45 (m, 4H), 7.35 – 7.30 (m, 1H), 7.02 (d, *J* = 9.2 Hz, 1H), 6.70 (d, *J* = 9.2 Hz, 1H), 4.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.9, 160.8, 142.1, 133.0, 132.9, 130.5, 130.4, 128.7, 128.5, 128.2, 124.5, 122.2, 118.5, 117.7, 114.2, 111.9, 53.3. **ESI-MS:** Calcd for $C_{19}H_{14}N_2O_2$: [M+H$^+$] 303.1128, found 303.1135.



(3-bromopyrido[2,3-*a*]indolizin-5-yl)(phenyl)methanone (**4fa**)

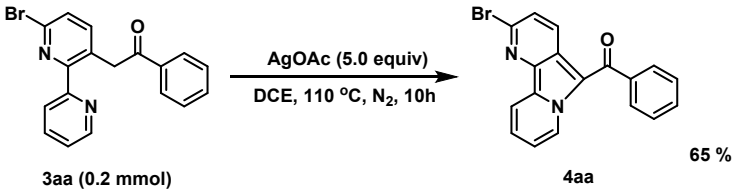
Yellow solid (16 mg, 22%); M.P.: 206-208 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 7.2 Hz, 1H), 8.57 – 8.55 (m, 2H), 7.69 – 7.62 (m, 4H), 7.58 – 7.50 (m, 3H), 7.25 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 146.2, 141.4, 134.1, 131.0, 129.2, 128.8, 128.7, 128.0, 126.7, 126.5, 120.2, 120.0, 117.9, 110.8. **ESI-MS:** Calcd for $C_{18}H_{11}BrN_2O$: [M+H$^+$] 351.0128, found 351.0128.

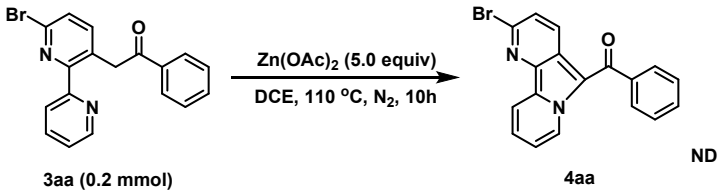


phenyl(pyrido[2',3':3,4]pyrrolo[2,1-*a*]isoquinolin-8-yl)methanone (**4ga**)

Yellow solid (15 mg, 24%); M.P.: 176-178 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.22 (d, *J* = 7.6 Hz, 1H), 9.99 – 9.96 (m, 1H), 8.73 (dd, *J* = 4.0, 1.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.76 – 7.69 (m, 3H), 7.64 – 7.59 (m, 2H), 7.57 – 7.52 (m, 2H), 7.25 – 7.21 (m, 1H), 7.18 – 7.14 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.3, 146.4, 142.0, 137.7, 130.9, 129.2, 128.6, 128.6, 127.8, 126.7, 126.2, 125.8, 125.7, 125.5, 121.6, 118.6, 112.8. **ESI-MS:** Calcd for $C_{22}H_{14}N_2O$: [M+H$^+$] 323.1179, found 323.1185.

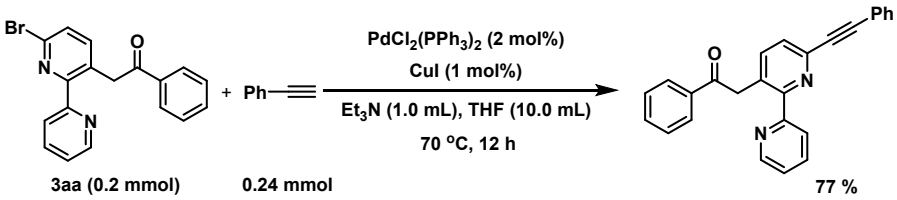
Control Experiment





A sealed tube contained **3aa** (70.6 mg, 0.2 mmol), AgOAc (166.91 mg, 1.0 mmol) was filled and purged with nitrogen gas three times. Then DCE (4.0 mL) was added to the system via syringe under a nitrogen atmosphere and the reaction was allowed to stir at 110 °C for 10 h. The reaction solution was concentrated in vacuum and the residue was purified by column chromatography on silica gel to afford the desired pure product **4aa** (46 mg, 65%) as a yellow solid, next replace the added AgOAc with $Zn(OAc)_2$ (183.48 mg, 1.0 mmol), and the product **4aa** was not detected.

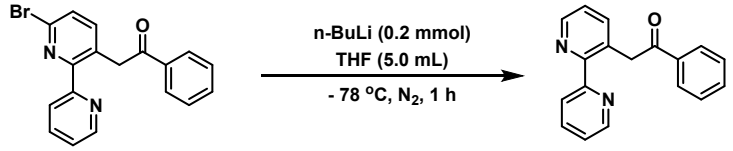
Synthetic Transformations:



A mixture of **3aa** (70.6 mg, 0.2 mmol), phenylacetylene (24.5 mg, 0.24 mmol), $PdCl_2(PPh_3)_2$ (2.8 mg, 2 mmol%), Et_3N (2.0 mL) and CuI (0.5 mg, 1 mmol%) in THF (10.0 mL) was heated at 70 °C overnight. The mixture was cooled to r.t., and the solvent was removed at reduced pressure. The residue was purified by silica gel chromatography to give **5** (58 mg, 77%) as a yellow solid.

M.P.: 121-122 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 1H), 8.14 – 8.12 (m, 1H), 7.99 – 7.96 (m, 2H), 7.78 – 7.73 (m, 1H), 7.66 – 7.61 (m, 3H), 7.59 – 7.54 (m, 2H), 7.49 – 7.44 (m, 2H), 7.39 – 7.34 (m, 3H), 7.16 – 7.11 (m, 1H), 4.73 (s, 2H). **^{13}C NMR** (100 MHz,

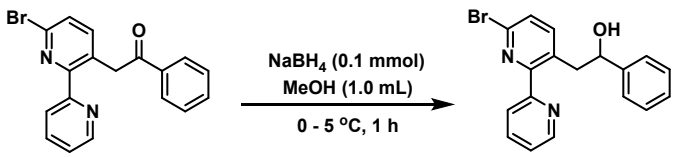
$CDCl_3$) δ 196.8, 157.2, 155.2, 147.4, 141.4, 141.1, 137.1, 136.8, 132.7, 132.0, 129.4, 128.8, 128.5, 128.3, 128.1, 126.6, 124.1, 123.0, 122.3, 88.8, 88.7, 43.6. **ESI-MS**: Calcd for $C_{26}H_{18}N_2O$: [M+H$^+$] 375.1492, found 375.1491.



3aa (0.2 mmol) 81 %

A 50.0 mL 3-neck flask was charged with **3aa** (70.6 mg, 0.2 mmol) in 5.0 mL THF under N_2, and cooled to - 78 °C with a acetone/liquid N_2 slush bath. A n-butyl llithium solution (0.3 mL, 0.4 mmol) was added dropwise to the slurry which changed color from white to orange. The temperature was then raised to - 78 °C and within one hour it became an orange solution. Then in sequence, 5.0 mL methanol and then 2.0 mL H_2O were added to the solution. The THF and methanol were removed by rotary evaporation and a yellow solid was isolated by vacuum filtration of the aqueous supernatent. The residue was purified by silica gel chromatography to give **6** (44 mg, 81%) as a white solid.

M.P.: 74-76 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.15 – 8.11 (m, 2H), 8.01 – 7.97 (m, 2H), 7.78 – 7.72 (m, 1H), 7.78 – 7.65 (m, 1H), 7.59 – 7.54 (m, 1H), 7.50 – 7.45 (m, 2H), 7.32 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.15 – 7.11 (m, 1H), 4.72 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.1, 157.9, 154.9, 147.8, 147.5, 140.9, 137.3, 136.7, 132.6, 129.9, 128.5, 128.2, 123.7, 123.1, 122.7, 43.8. **ESI-MS**: Calcd for $C_{18}H_{14}N_2O$: [M+H$^+$] 275.1179, found 275.1188.

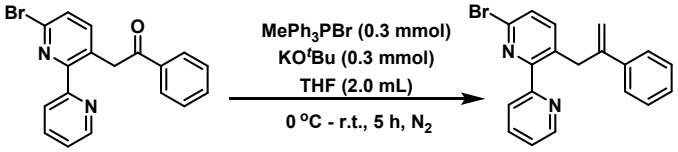


3aa (0.2 mmol) 90 %

In a two-necked round bottomed flask **3aa** (70.6 mg, 0.2 mmol) was dissolved in methanol (1.0 mL) under a nitrogen atmosphere at ice-water temperature. Next, sodium borohydride(3.8 mg, 0.1 mmol) was added portionwise with stirring at a rate sufficient enough to maintain the reaction temperature at 0 – 5 °C. The reaction mixture was stirred for 1 h. Next, brine(1.0 mL) was added and the resultant suspension was stirred at room temperature for 10 min. The reaction mixture was diluted by the addition of AcOEt (5.0 mL) and distilled

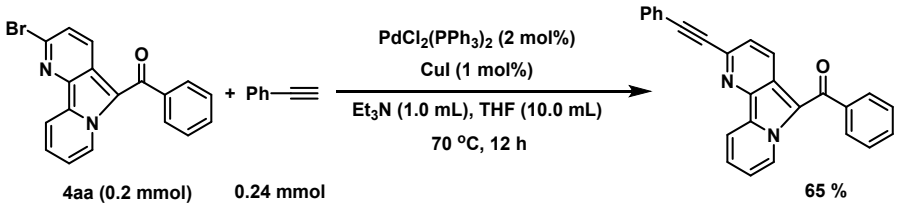
water (3.0 mL),and the layers were separated. The aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine and dried over $MgSO_4$. Next, the solvent was evaporated to dryness leaving a crude product, the residue was purified by column chromatography to give **7** (64 mg, 90%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.45 – 7.41 (m, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 5.13 – 5.09 (m, 1H), 3.15 (d, *J* = 2.8 Hz, 1H), 3.14 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 155.6, 146.7, 145.4, 142.2, 139.1, 138.2, 132.4, 128.3, 127.7, 127.1, 125.7, 125.6, 123.8, 74.6, 41.2. **ESI-MS**: Calcd for $C_{18}H_{15}BrN_2O$: [M+H$^+$] 355.0441, found 355.0442.



A mixture of $MePPh_3Br$ (107.2 mg, 0.3 mmol) and KO^{t}Bu (33.7 mg, 0.3 mmol) in THF (2.0 mL) was stirred at room temperature for 1 h. Then **3aa** (70.6 mg, 0.2 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **8** (42 mg, 60%) as a colorless oil.

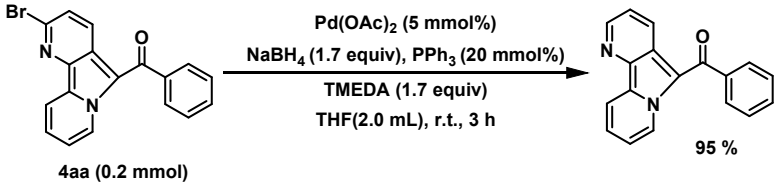
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.56 (m, 1H), 7.77 – 7.71 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.17 – 7.13 (m, 2H), 5.34 (s, 1H), 4.81 (d, *J* = 1.2 Hz, 1H), 4.14 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3, 156.8, 148.4, 146.2, 141.3, 140.2, 138.9, 136.8, 133.4, 128.3, 127.6, 127.5, 126.1, 124.5, 123.2, 114.9, 37.4. **ESI-MS**: Calcd for $C_{19}H_{15}BrN_2$: [M+H$^+$] 351.0491, found 351.0493.



A mixture of **4aa** (70.2 mg, 0.2 mmol), phenylacetylene (24.5 mg, 0.24 mmol), $PdCl_2(PPh_3)_2$ (2.8 mg, 2 mmol%), Et_3N (2.0 mL) and CuI (0.5 mg, 1 mmol%) in THF (10.0 mL) was heated at 70 °C overnight. The mixture was cooled to r.t., and the solvent was

removed at reduced pressure. The residue was purified by silica gel chromatography to give **9** (48 mg, 65%) as a yellow solid.

M.P.: 226-227 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.56 (d, *J* = 6.8 Hz, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.64 – 7.46 (m, 7H), 7.39 – 7.34 (m, 4H), 7.11 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.6, 141.8, 138.2, 136.2, 134.0, 132.1, 130.8, 129.2, 128.9, 128.7, 128.4, 128.2, 126.9, 126.5, 126.4, 124.6, 122.4, 120.3, 118.4, 111.9, 89.6, 89.4. **ESI-MS**: Calcd for $C_{26}H_{16}N_2O$: [M+H$^+$] 373.1335, found 373.1341.



A mixture of the **3aa** (35.1 mg, 0.1 mmol) in anhydrous THF (2.0 mL) was degassed by bubbling argon for few minutes. Then, $Pd(OAc)_2$ (1.1 mg, 0.005 mmol), PPh_3 (5.3 mg, 0.02 mmol), TMEDA (19.9 mg, 0.17 mmol) and finally $NaBH_4$ (6.4 mg, 0.17 mmol) were introduced in sequence. The mixture was stirred at room temperature under argon for 1 h. The residue was taken up in brine and extracted with ethyl acetate. The organic phase was separated, dried (Na_2SO_4), the solvent was evaporated and the residue was purified by column chromatography to give **10** (25 mg, 90%) as a yellow solid.

M.P.: 137-139 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.60 (d, *J* = 7.2 Hz, 1H), 8.58 – 8.55 (m, 2H), 7.67 – 7.64 (m, 2H), 7.60 – 7.44 (m, 5H), 7.17 – 7.10 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.3, 145.4, 141.9, 136.1, 134.3, 130.4, 129.0, 128.6, 128.0, 127.0, 125.9, 125.8, 122.7, 119.9, 117.8, 111.4. **ESI-MS**: Calcd for $C_{18}H_{12}N_2O$: [M+H$^+$] 273.1022, found 273.1025.

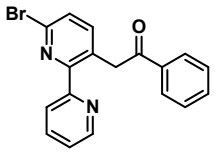
References:

[1] S. Wu, Z. Wang, Y. Bao, C. Chen, K. Liu, and B. Zhu, *Chem. Commun.*, 2020, **56**, 4408−4411.

[2] Y. Xu, X. Zhou, G. Zheng and X. Li, *Org. Lett.*, 2017, **19**, 5256−5259.

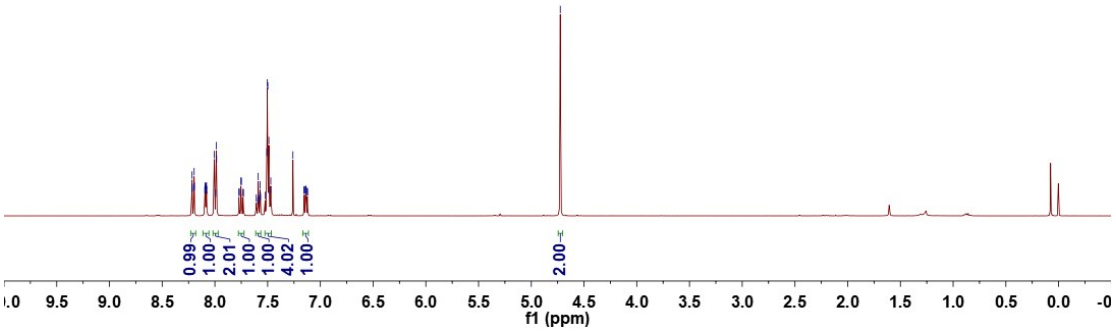
[3] A. G. Talero, B. S. Martins and A. C. B. Burtoloso, *Org. Lett.*, 2018, **20**, 7206−7211.

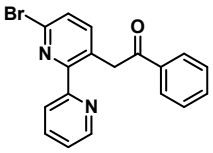
NMR Spectra



3aa

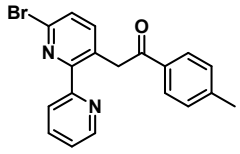
^{1}H NMR (400 MHz, $CDCl_3$)





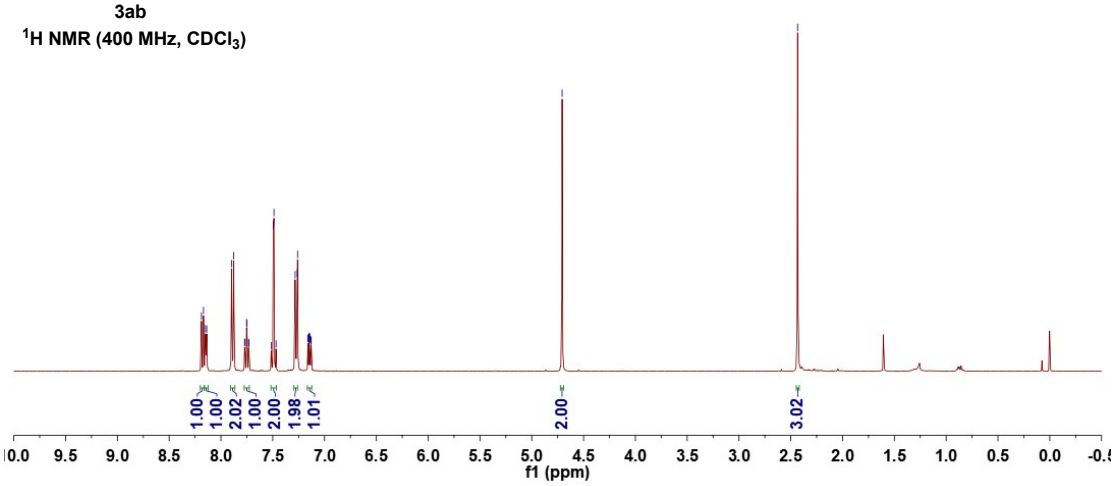
3aa

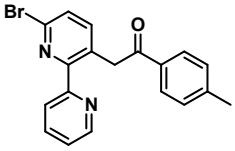
^{13}C NMR (100 MHz, $CDCl_3$)



3ab

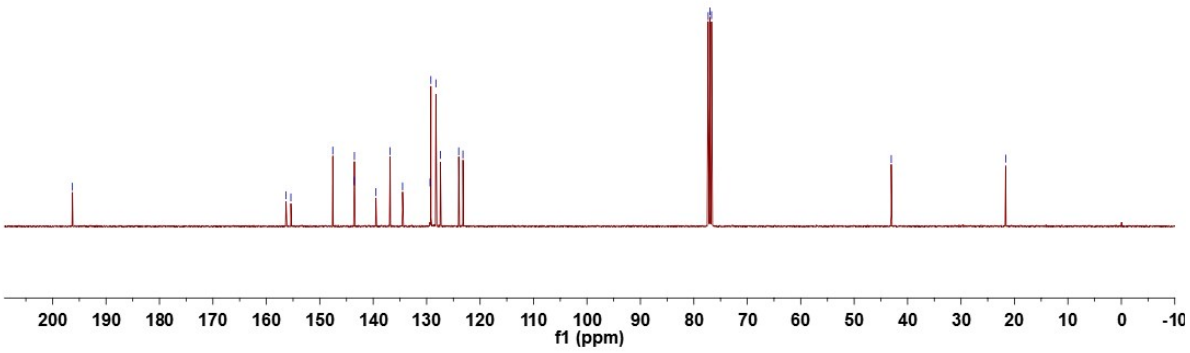
^{1}H NMR (400 MHz, $CDCl_3$)

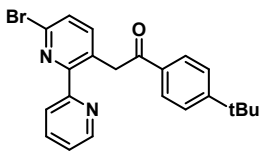




3ab

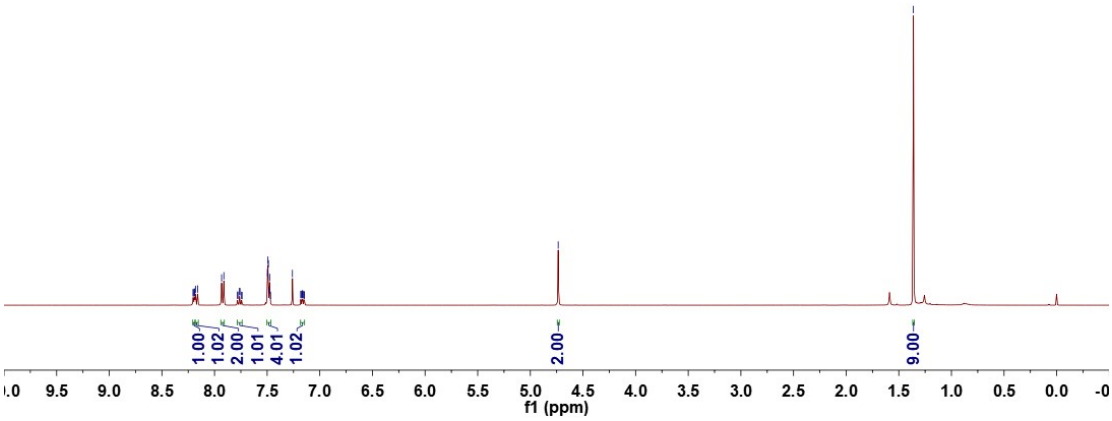
^{13}C NMR (100 MHz, $CDCl_3$)

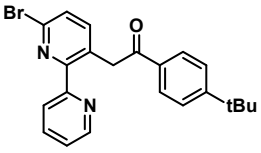




3ac

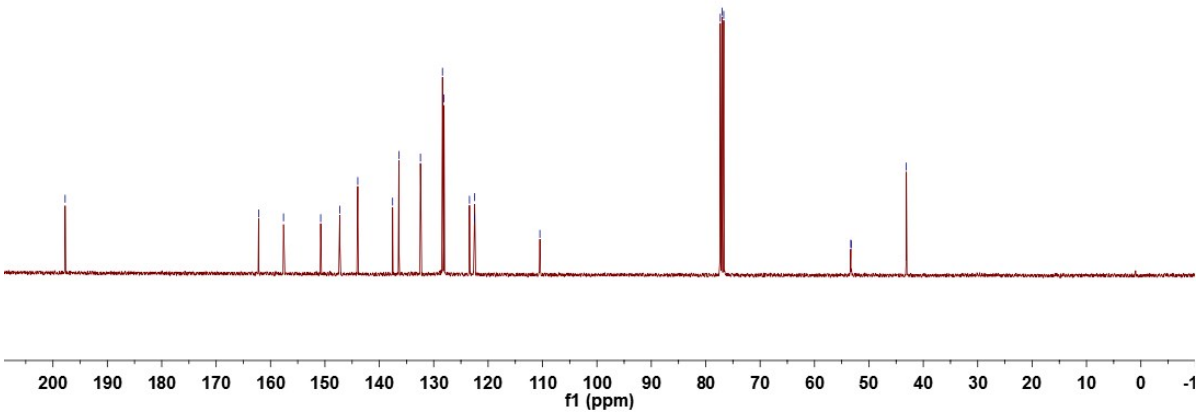
^{1}H NMR (400 MHz, $CDCl_3$)

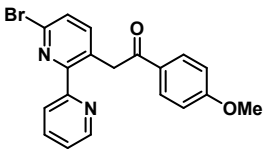




3ac

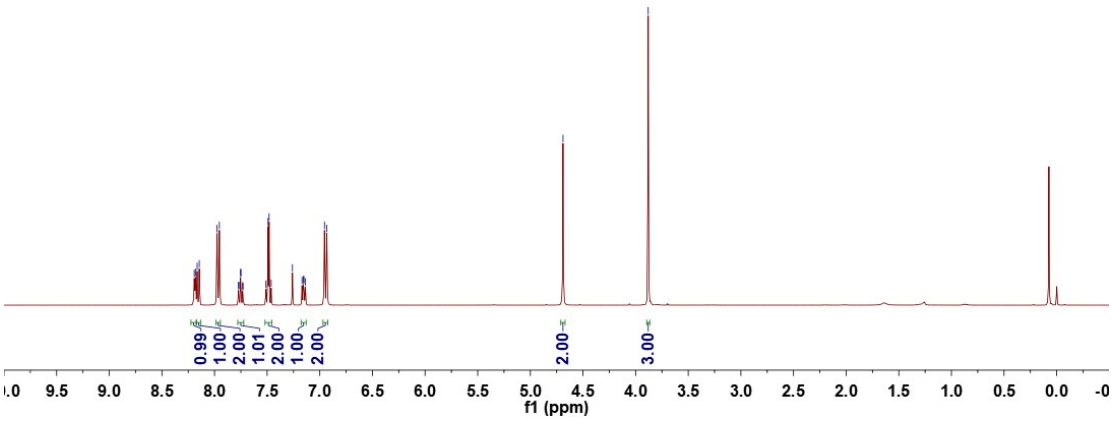
^{13}C NMR (100 MHz, $CDCl_3$)

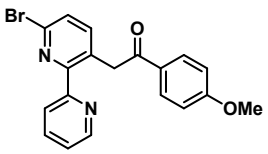




3ad

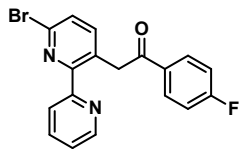
^{1}H NMR (400 MHz, $CDCl_3$)





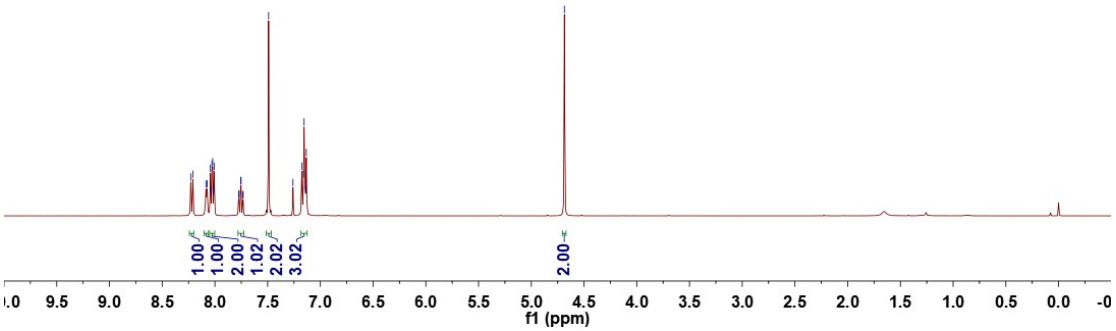
3ad

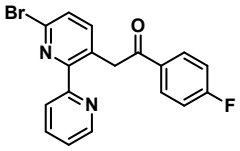
^{13}C NMR (100 MHz, $CDCl_3$)



3ae

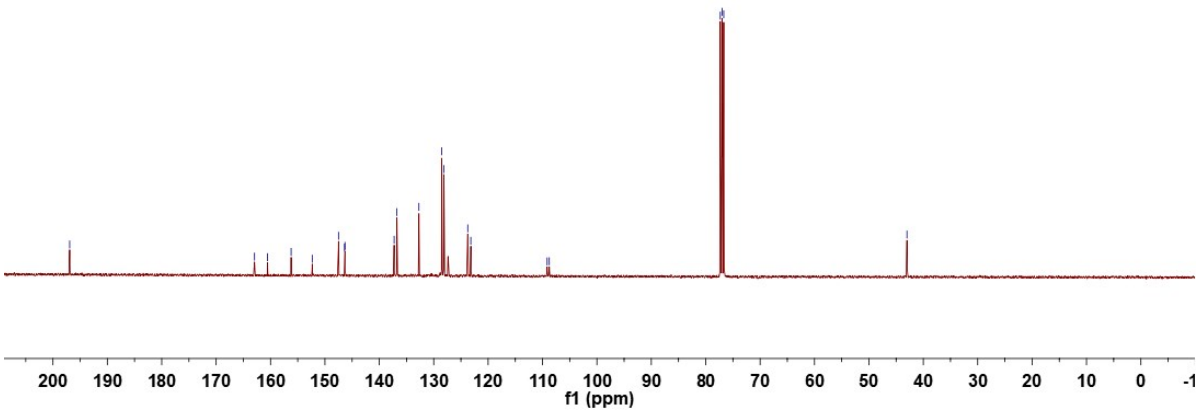
^{1}H NMR (400 MHz, $CDCl_3$)

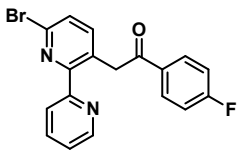




3ae

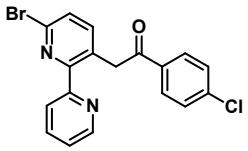
^{13}C NMR (100 MHz, $CDCl_3$)





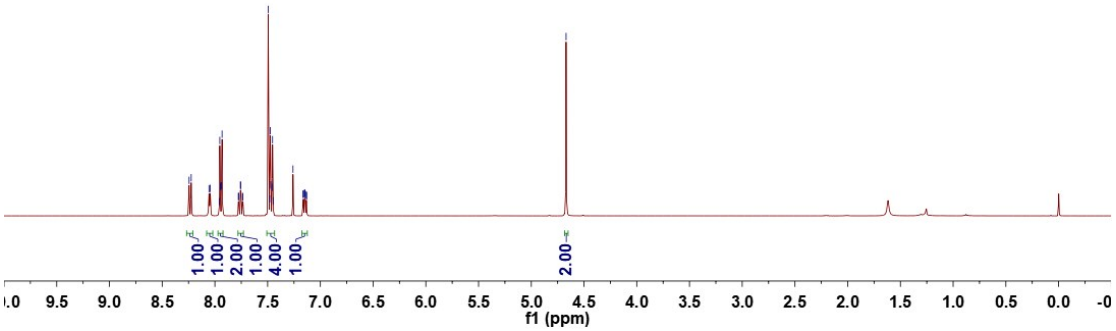
3ae

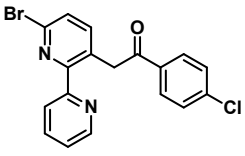
^{19}F NMR (376 MHz, $CDCl_3$)



3af

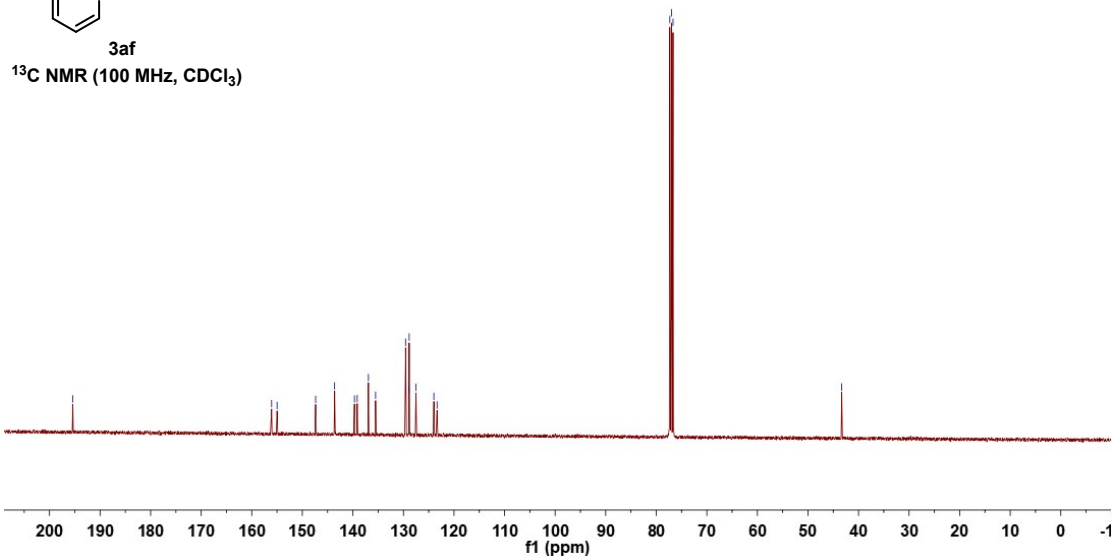
^{1}H NMR (400 MHz, $CDCl_3$)

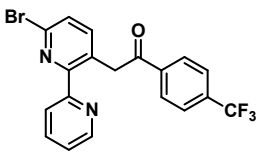




3af

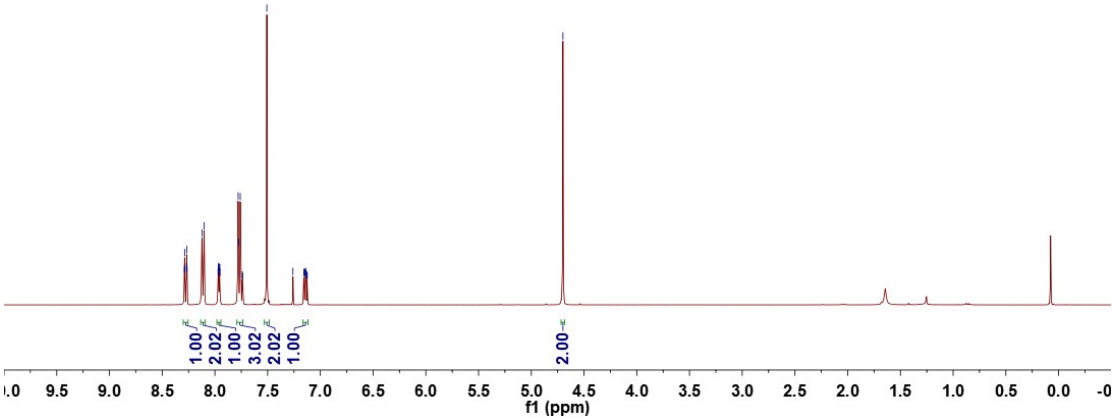
^{13}C NMR (100 MHz, $CDCl_3$)

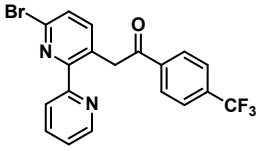




3ag

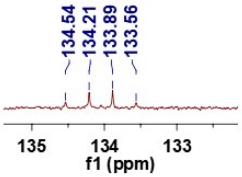
^{1}H NMR (400 MHz, $CDCl_3$)

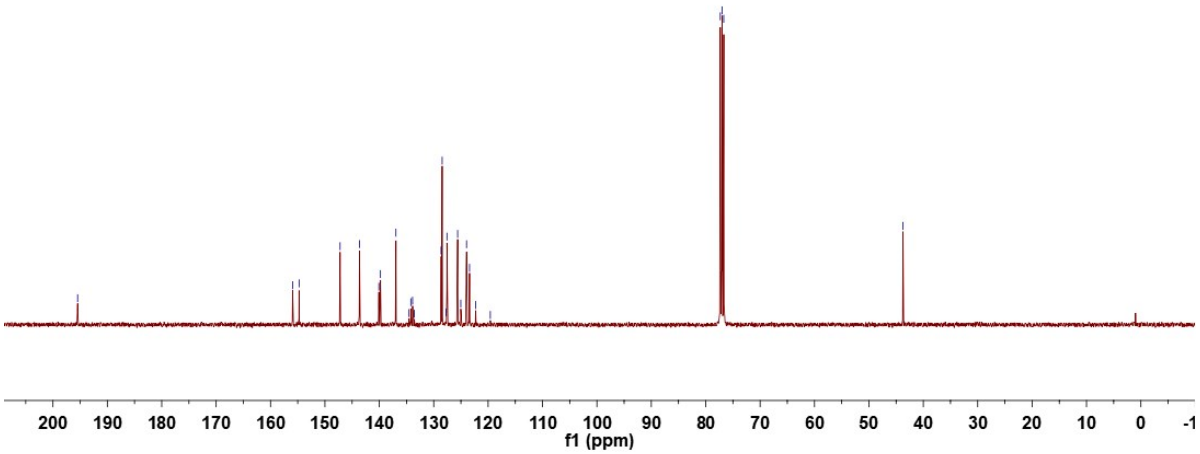


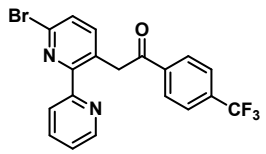


3ag

^{13}C NMR (100 MHz, $CDCl_3$)

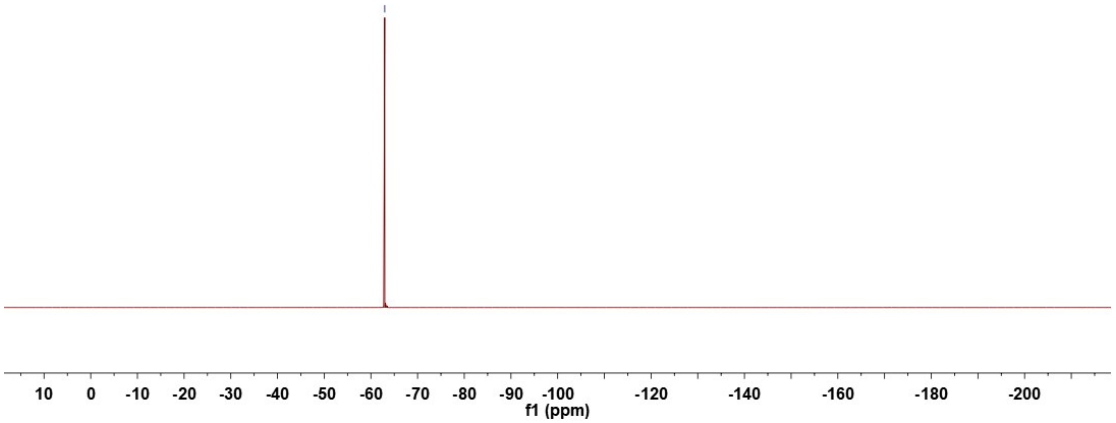


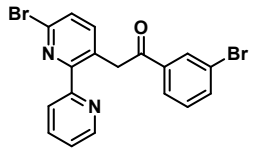




3ag

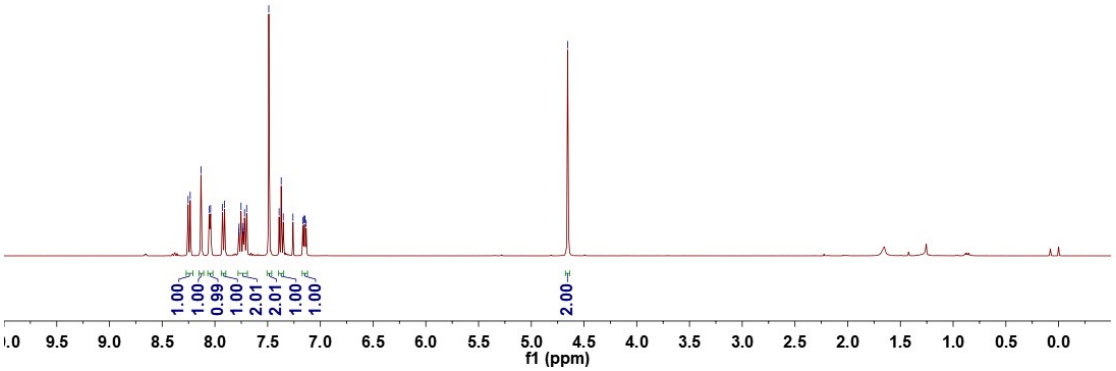
^{19}F NMR (376 MHz, $CDCl_3$)

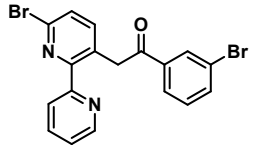




3ah

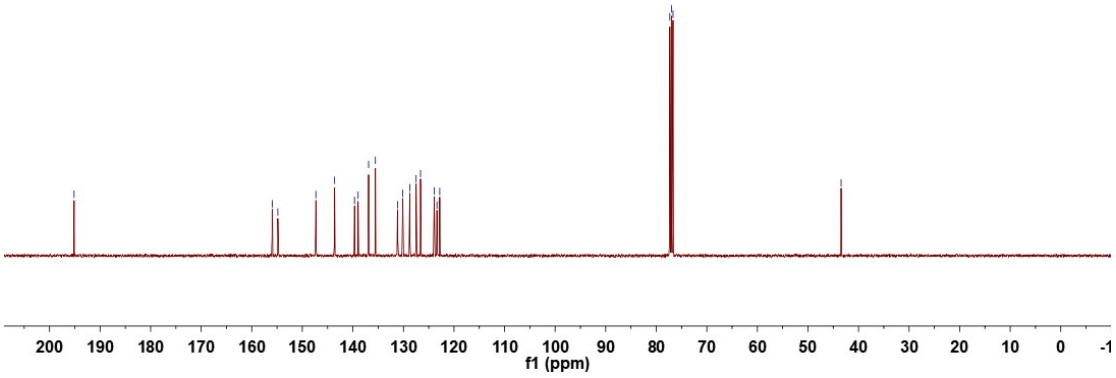
^{1}H NMR (400 MHz, $CDCl_3$)





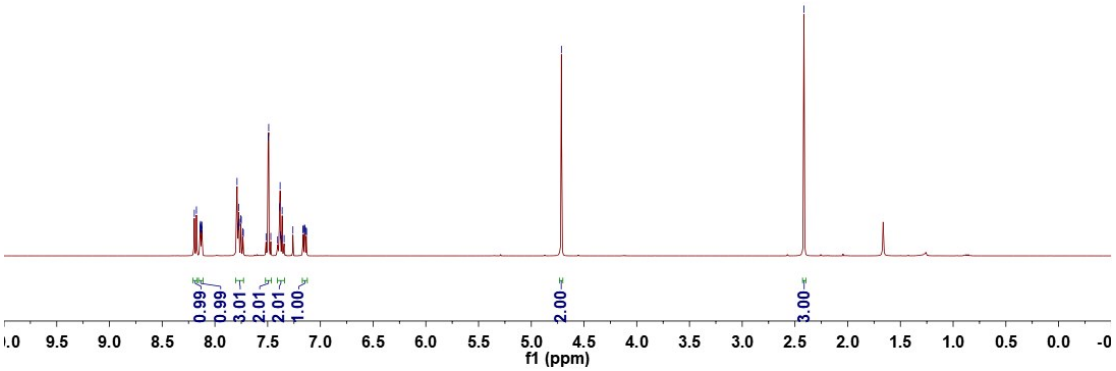
3ah

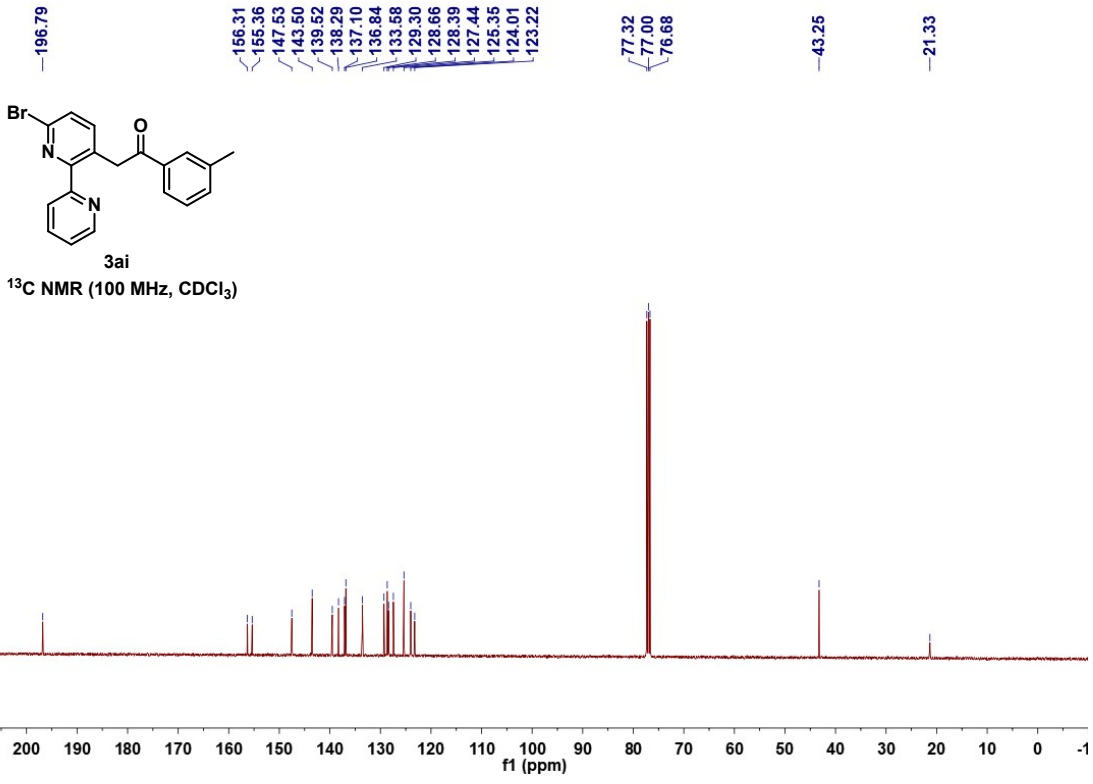
^{13}C NMR (100 MHz, $CDCl_3$)



3ai

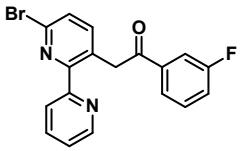
^{1}H NMR (400 MHz, $CDCl_3$)





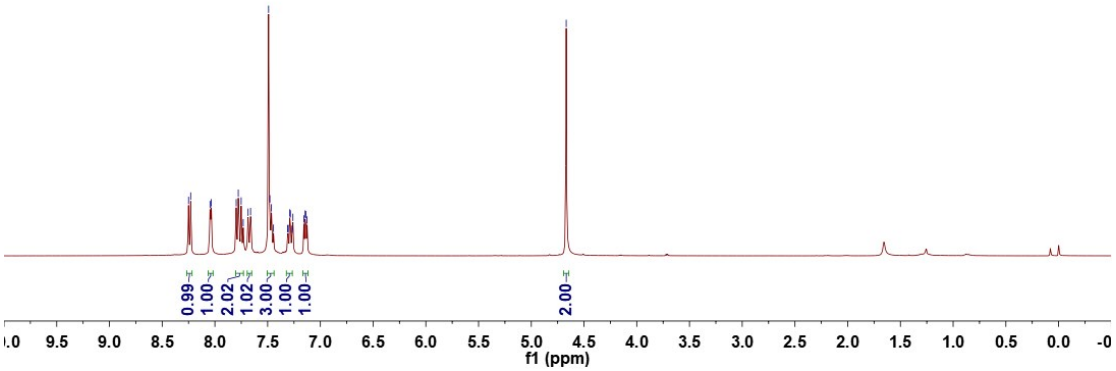
3ai

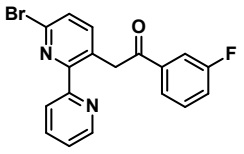
^{13}C NMR (100 MHz, $CDCl_3$)



3aj

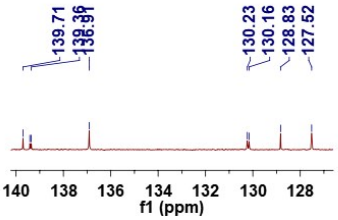
^{1}H NMR (400 MHz, $CDCl_3$)

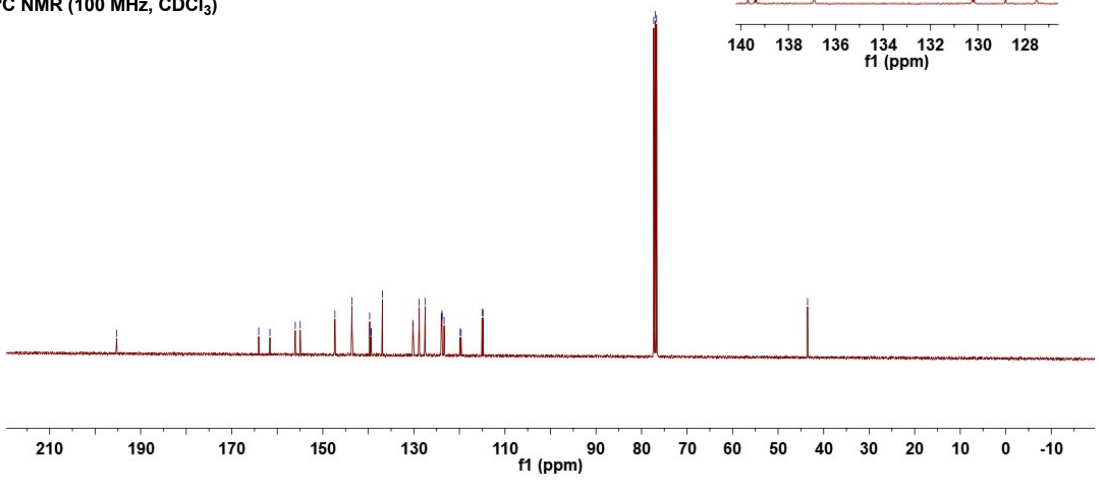


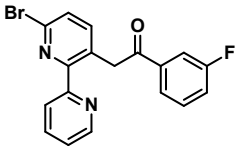


3aj

^{13}C NMR (100 MHz, $CDCl_3$)

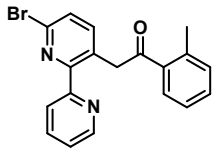






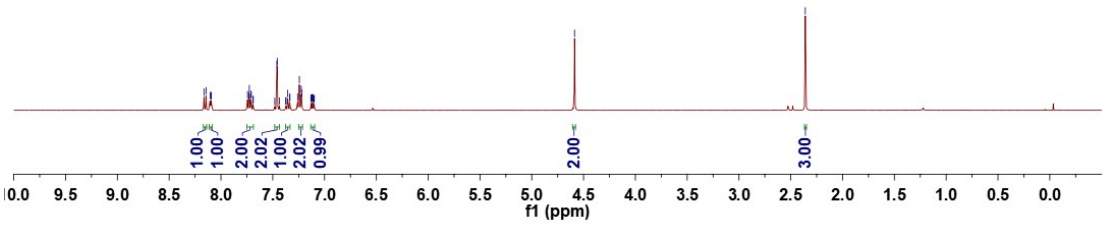
3aj

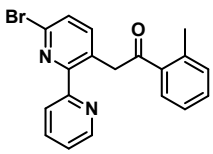
^{19}F NMR (376 MHz, $CDCl_3$)



3ak

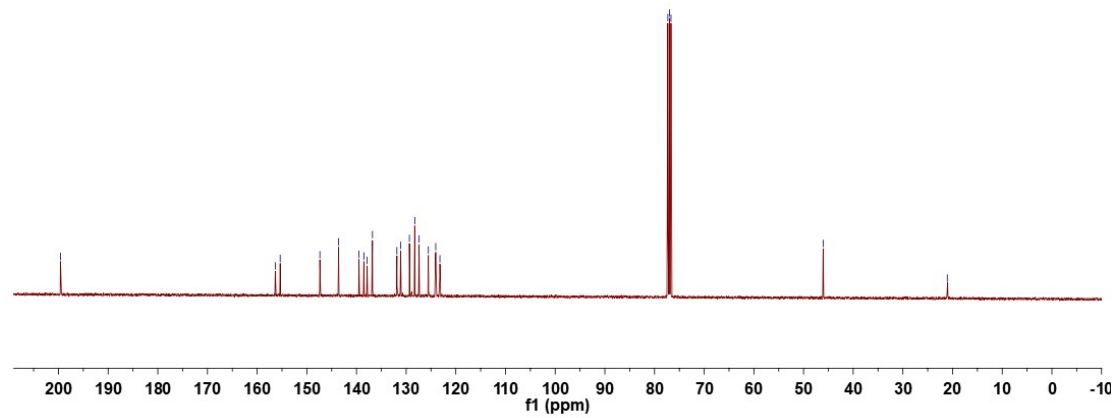
^{1}H NMR (400 MHz, $CDCl_3$)

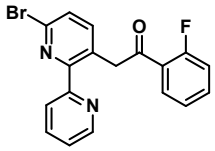




3ak

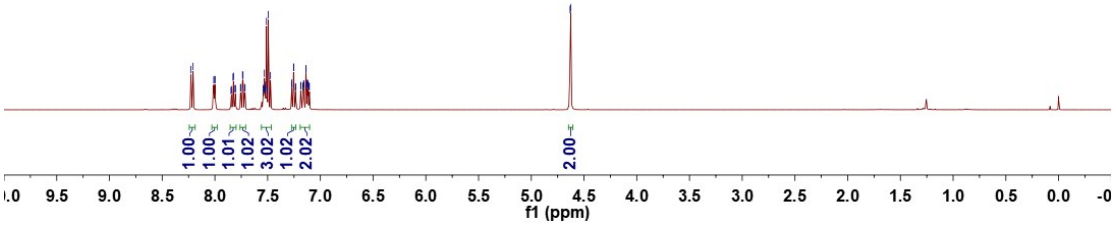
^{13}C NMR (100 MHz, $CDCl_3$)

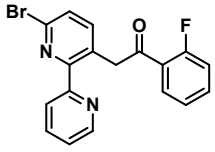




3al

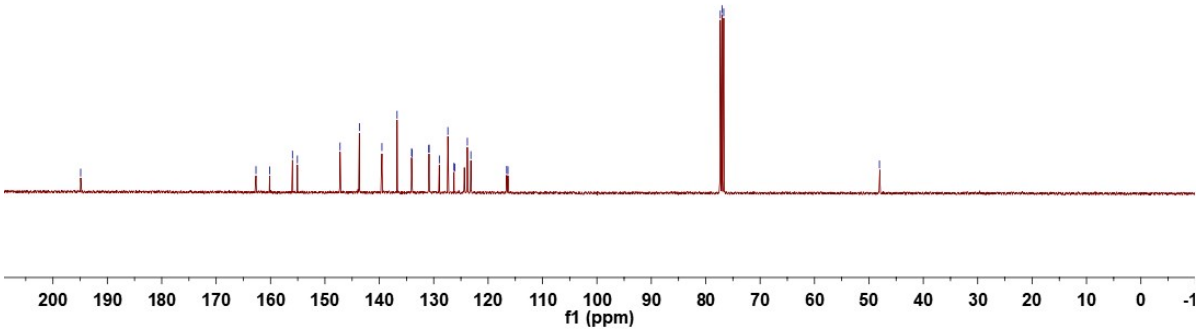
^{1}H NMR (400 MHz, $CDCl_3$)

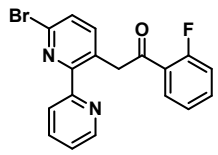




3al

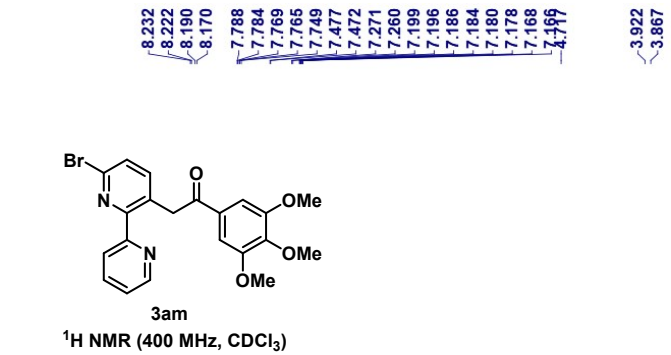
^{13}C NMR (100 MHz, $CDCl_3$)





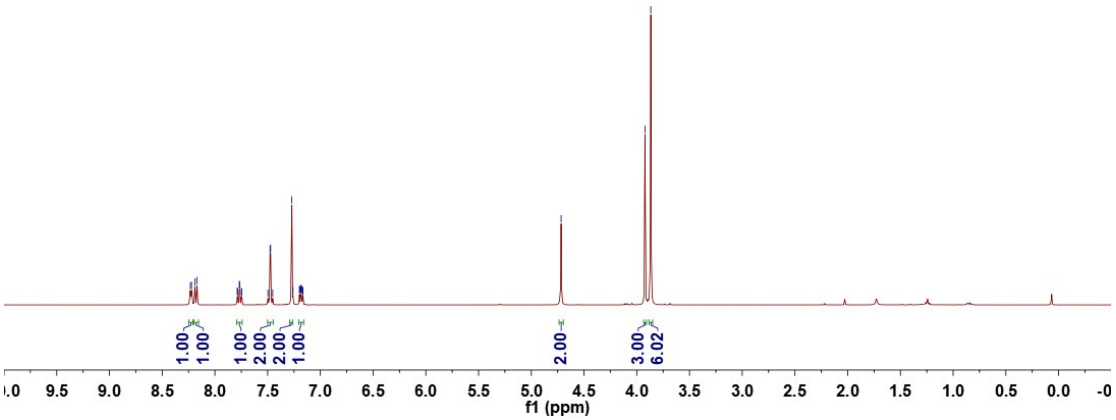
3al

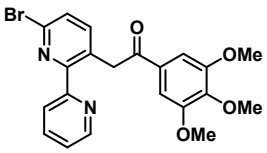
^{19}F NMR (376 MHz, $CDCl_3$)



3am

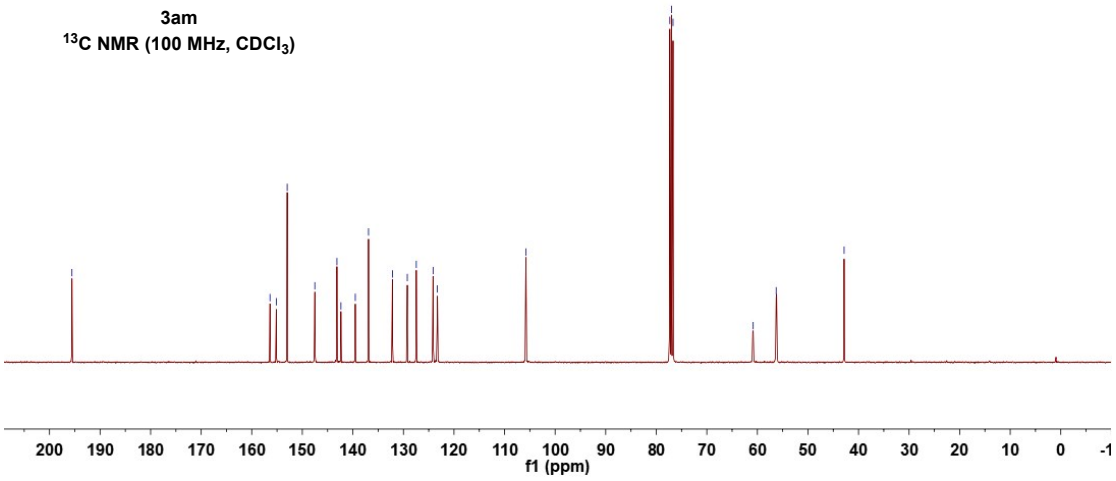
^{1}H NMR (400 MHz, $CDCl_3$)

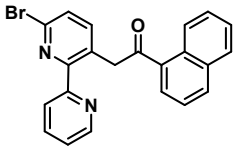




3am

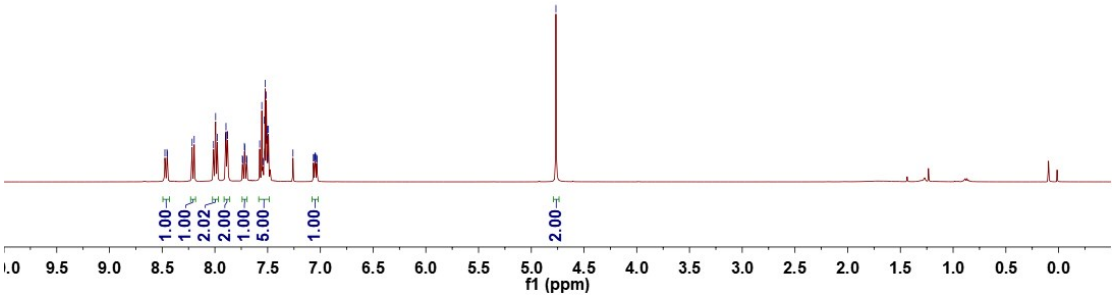
^{13}C NMR (100 MHz, $CDCl_3$)

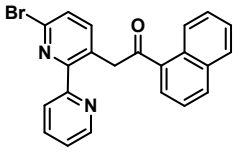




3an

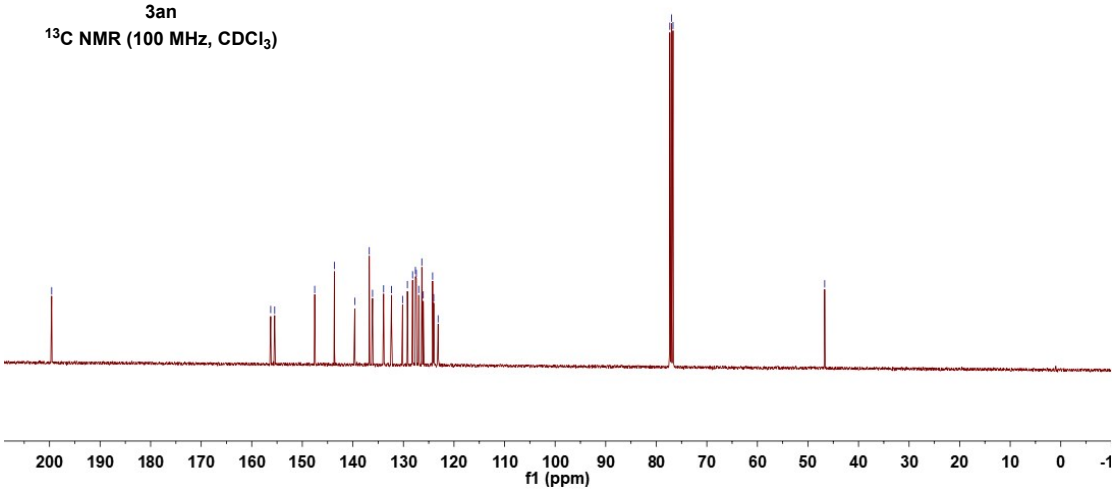
^{1}H NMR (400 MHz, $CDCl_3$)

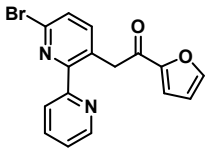




3an

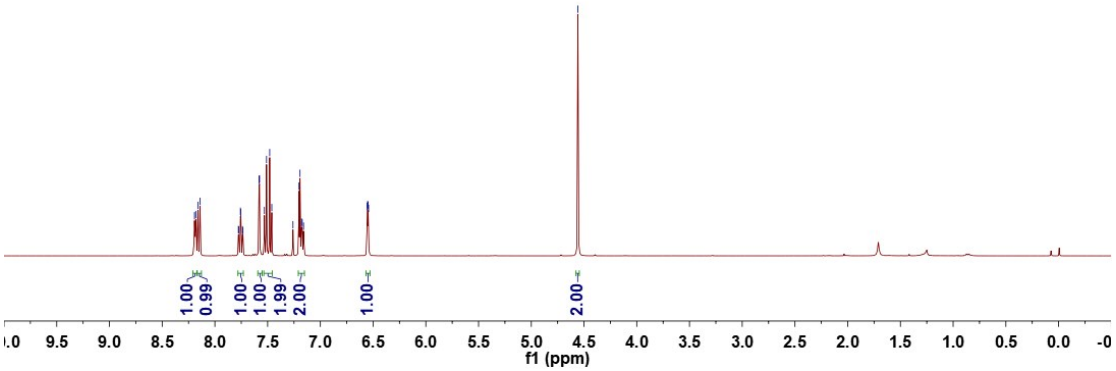
^{13}C NMR (100 MHz, $CDCl_3$)

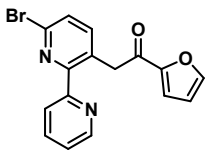




3ao

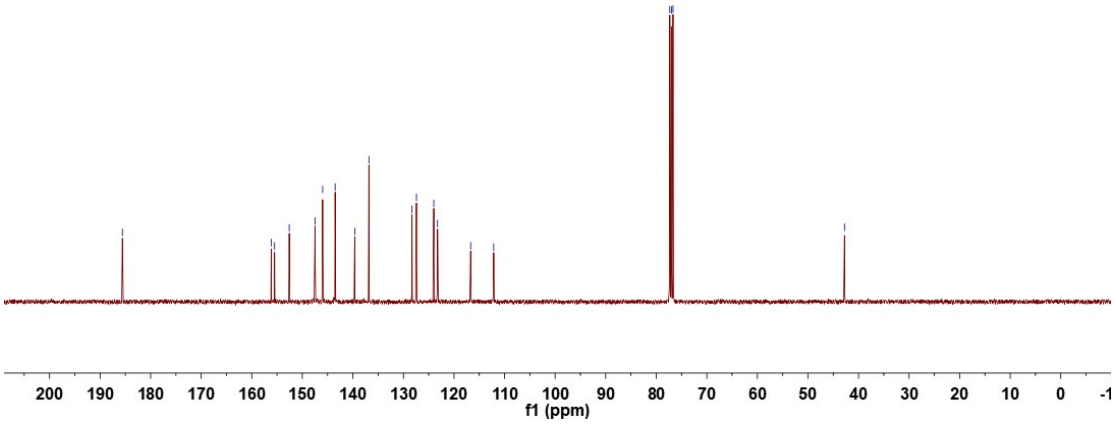
^{1}H NMR (400 MHz, $CDCl_3$)

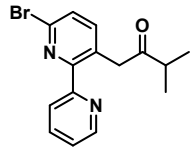




3ao

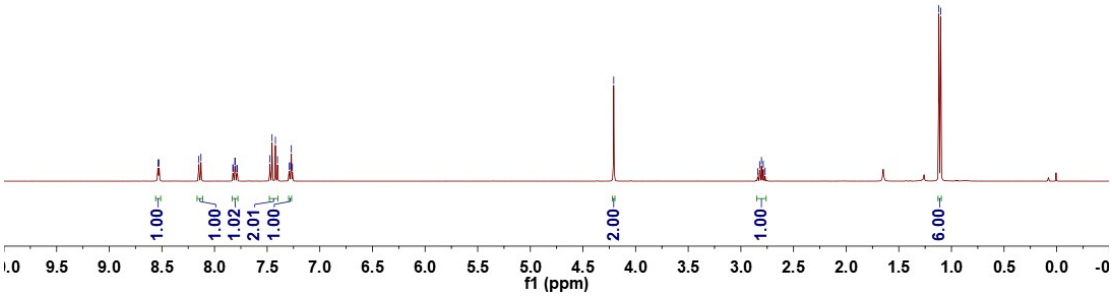
^{13}C NMR (100 MHz, $CDCl_3$)

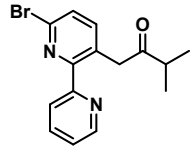




3ap

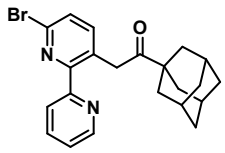
^{1}H NMR (400 MHz, $CDCl_3$)





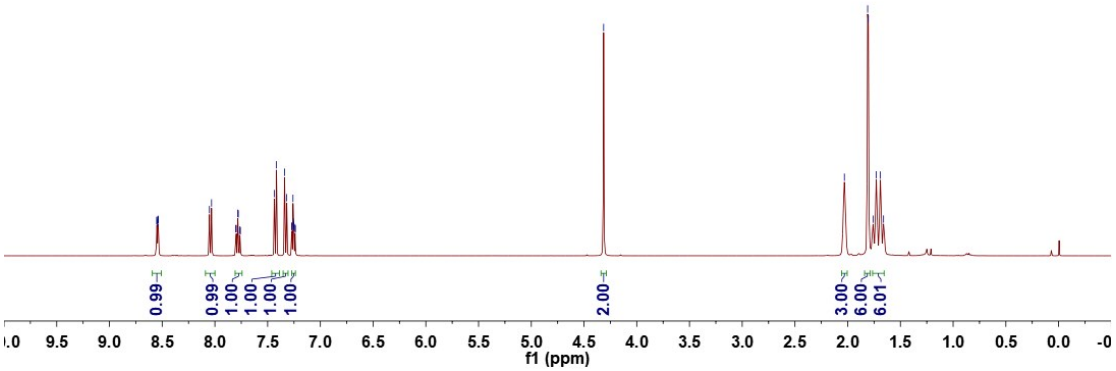
3ap

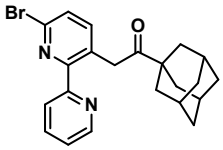
^{13}C NMR (100 MHz, $CDCl_3$)



3aq

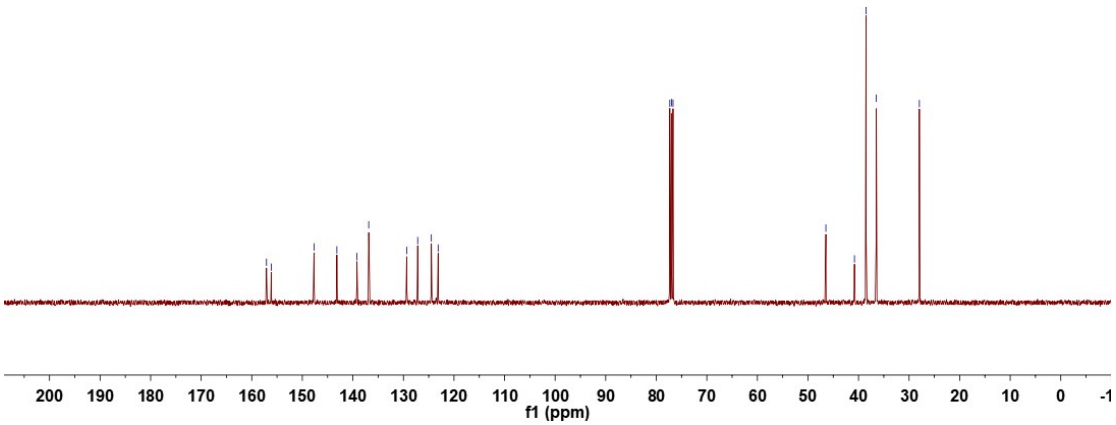
^{1}H NMR (400 MHz, $CDCl_3$)

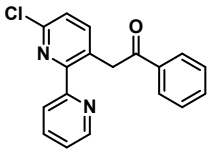




3aq

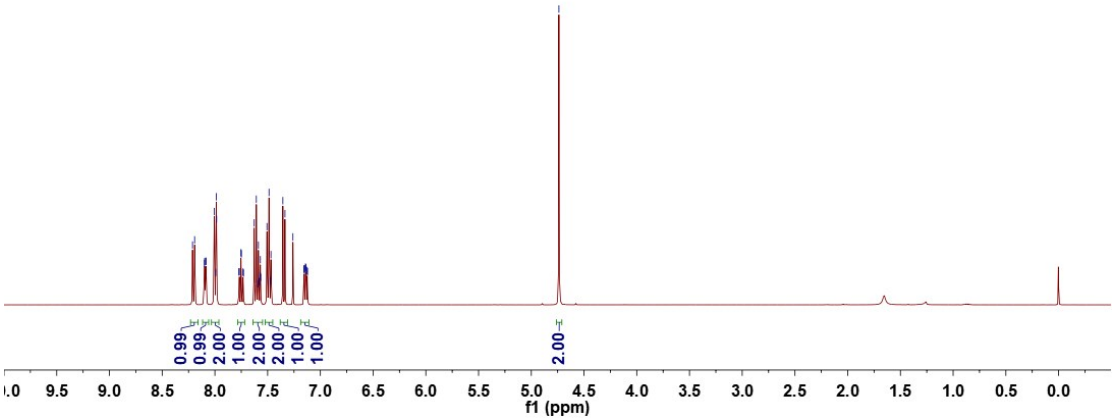
^{13}C NMR (100 MHz, $CDCl_3$)

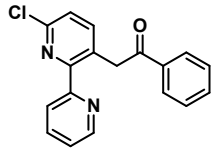




3ba

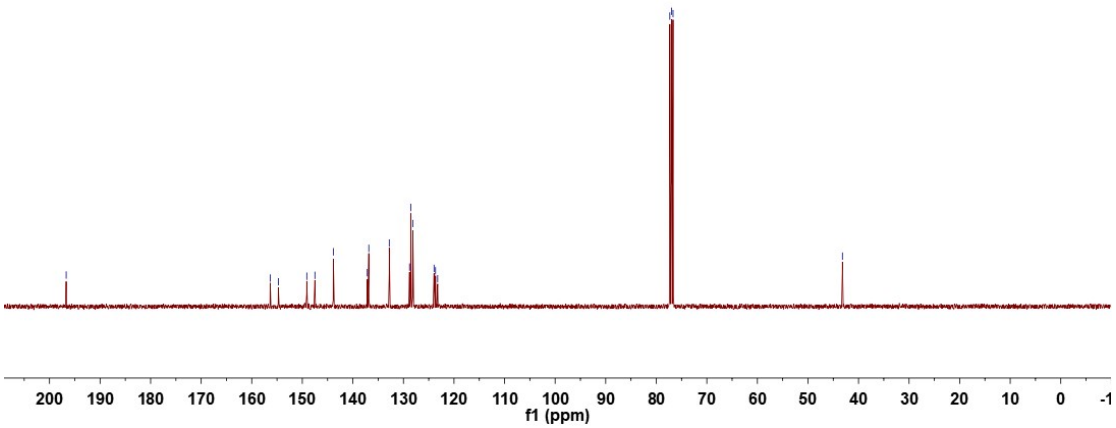
^{1}H NMR (400 MHz, $CDCl_3$)

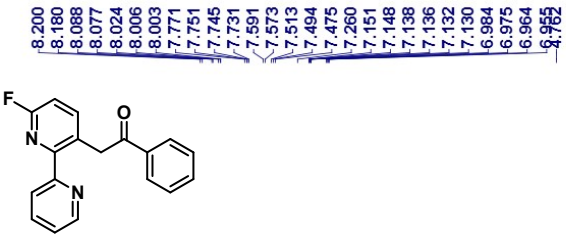




3ba

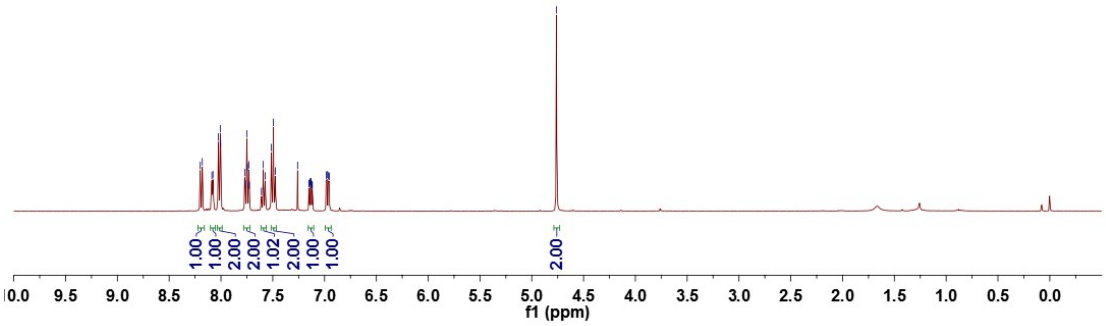
^{13}C NMR (100 MHz, $CDCl_3$)

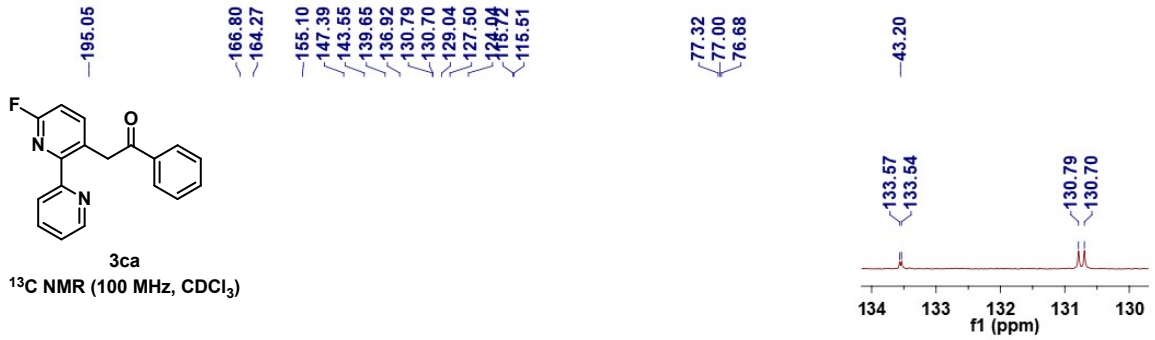




3ca

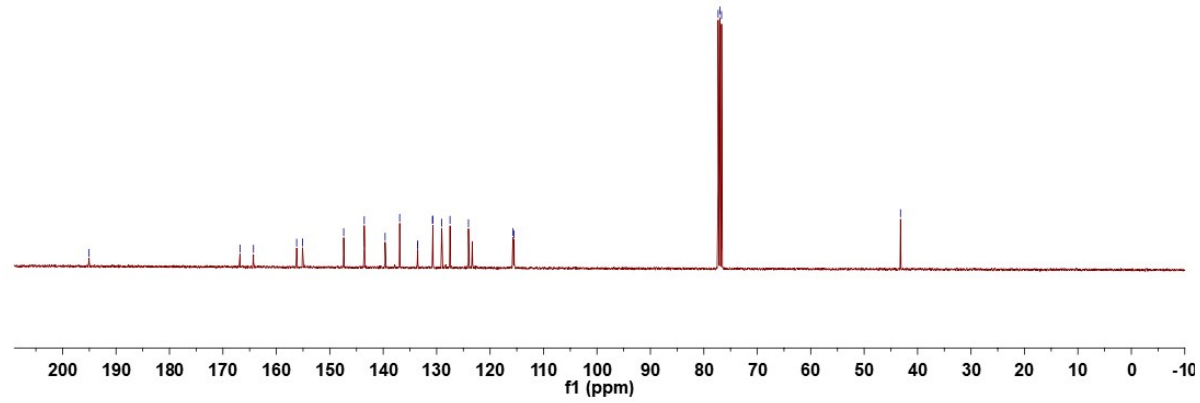
^{1}H NMR (400 MHz, $CDCl_3$)

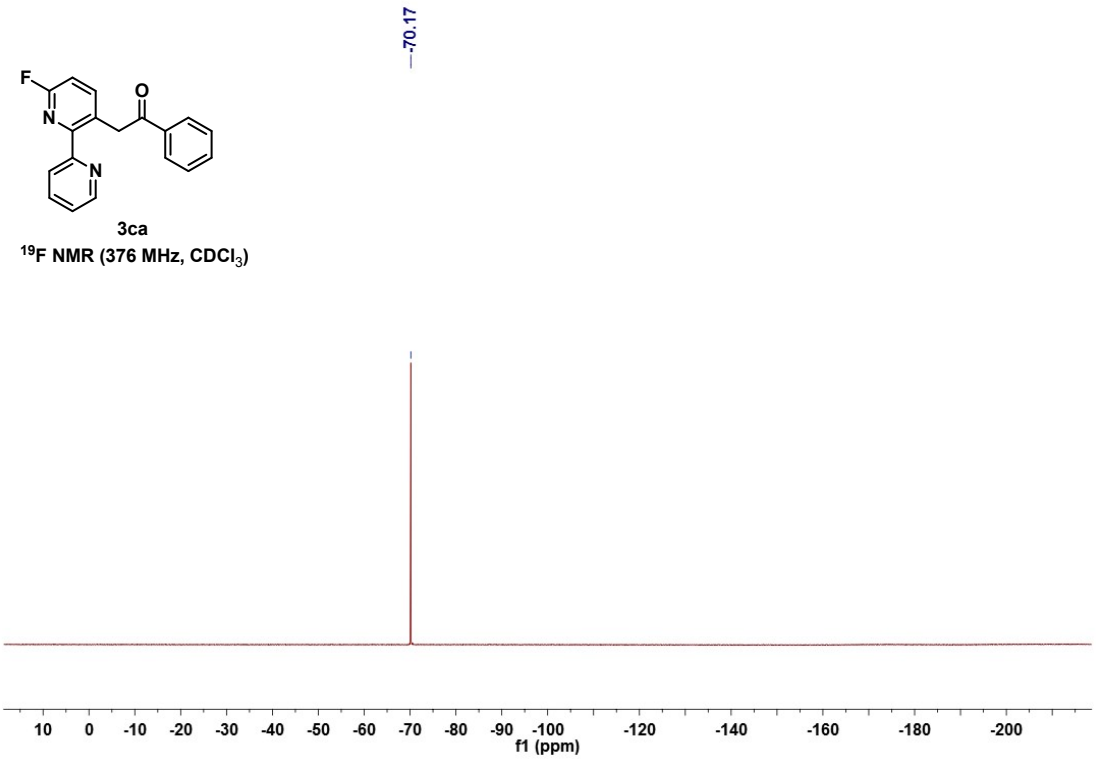




3ca

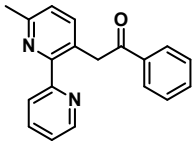
^{13}C NMR (100 MHz, $CDCl_3$)





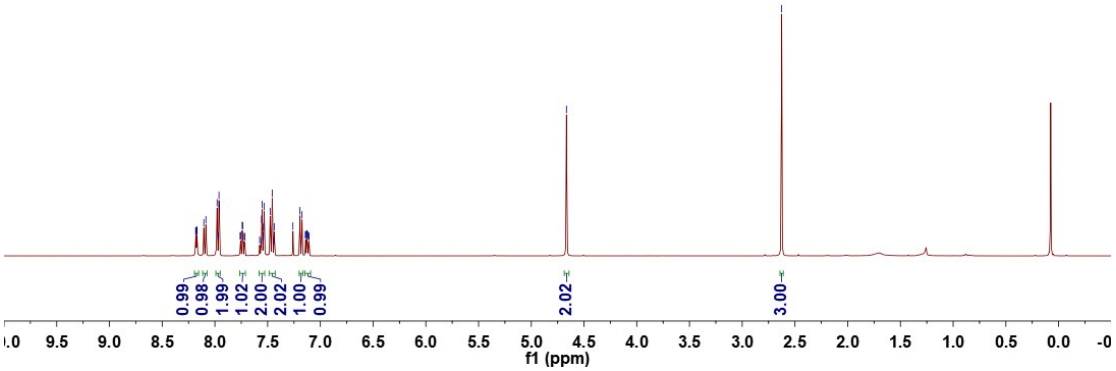
3ca

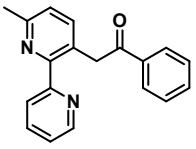
^{19}F NMR (376 MHz, $CDCl_3$)



3da

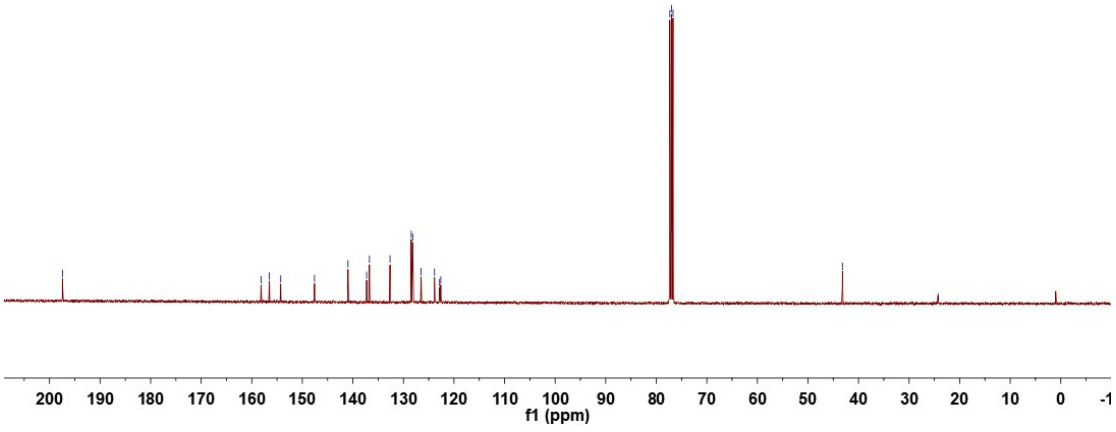
^{1}H NMR (400 MHz, $CDCl_3$)

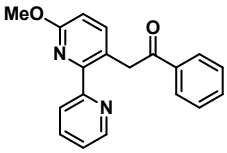




3da

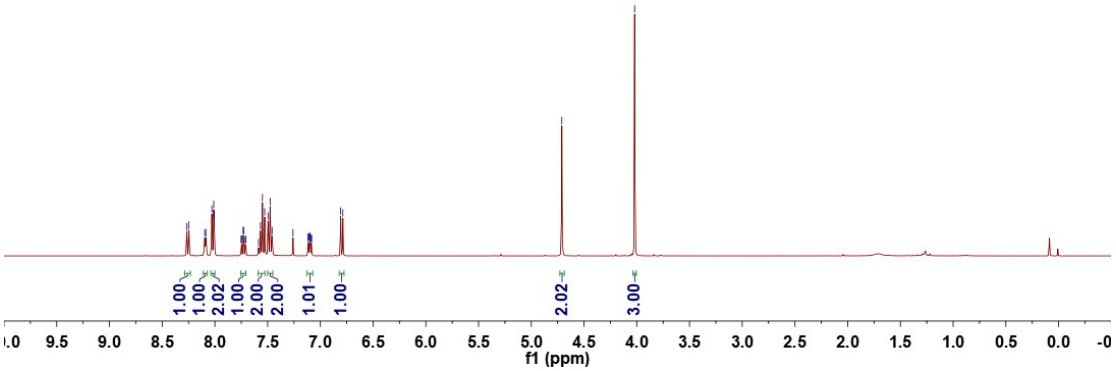
^{13}C NMR (100 MHz, $CDCl_3$)

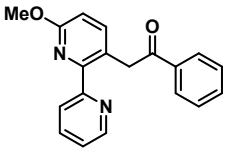




3ea

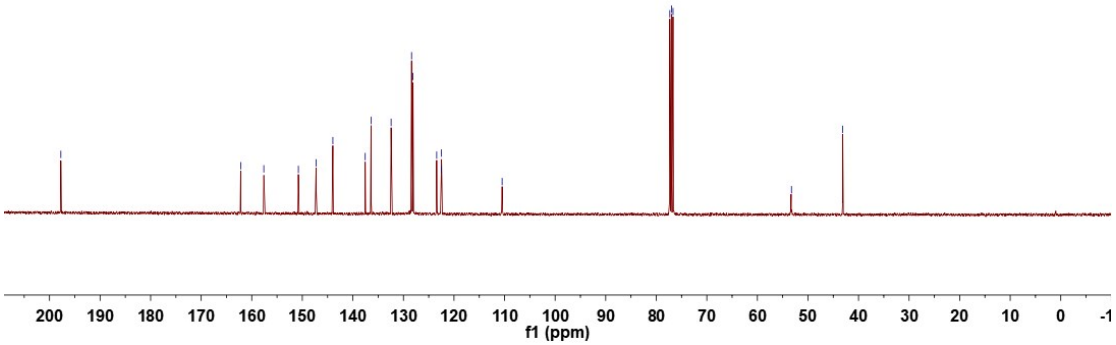
^{1}H NMR (400 MHz, $CDCl_3$)

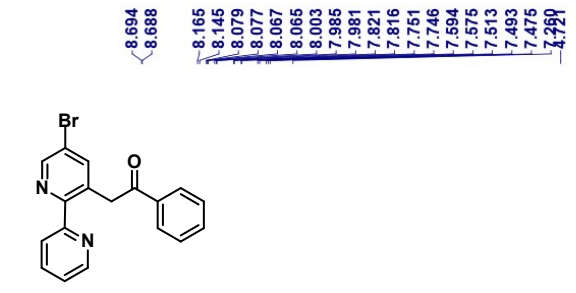




3ea

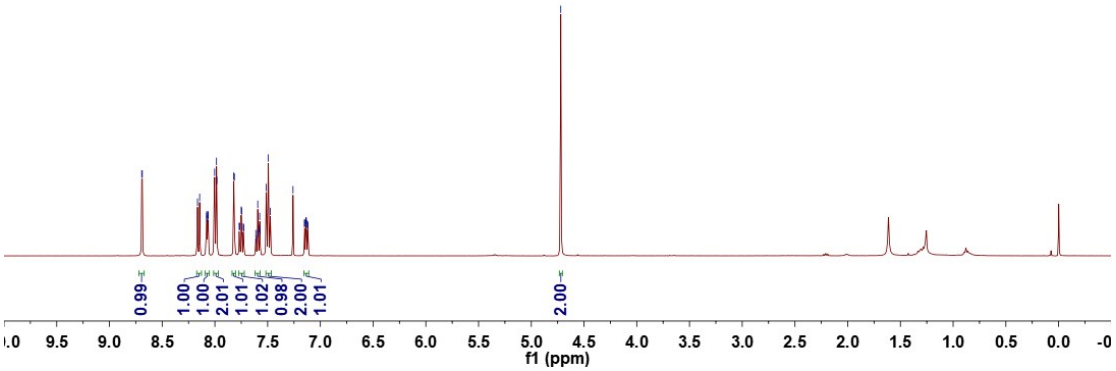
^{13}C NMR (100 MHz, $CDCl_3$)

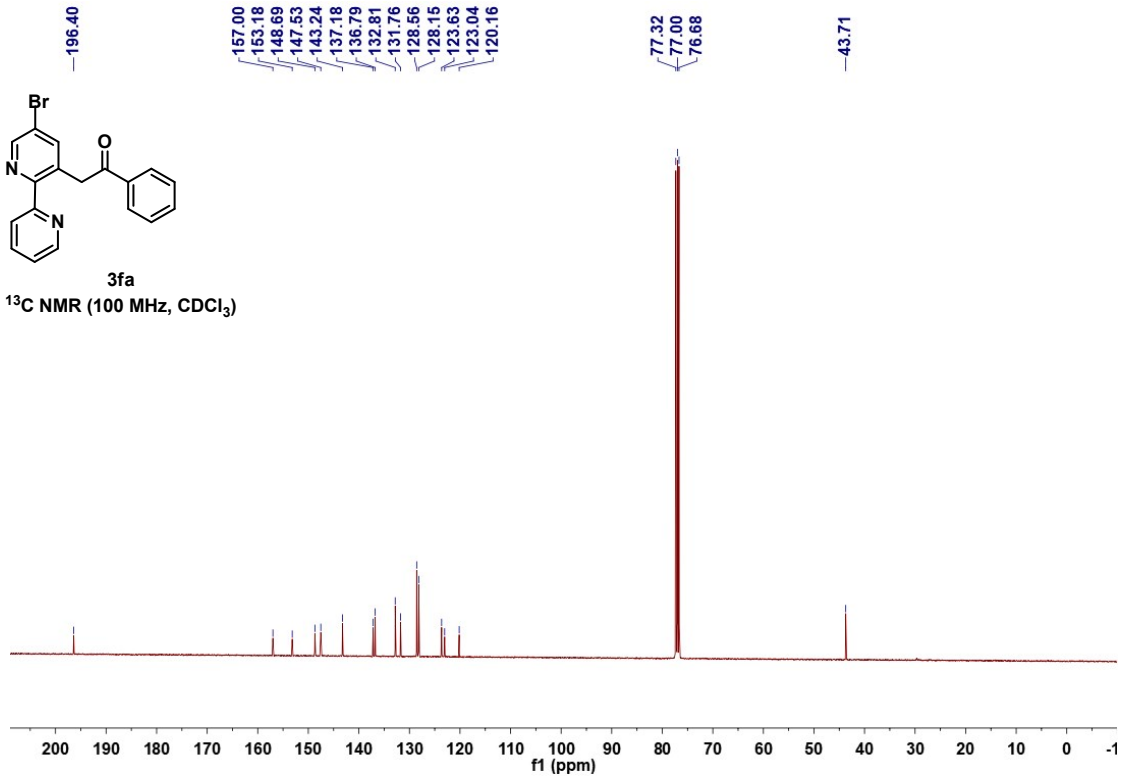




3fa

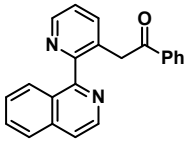
^{1}H NMR (400 MHz, $CDCl_3$)





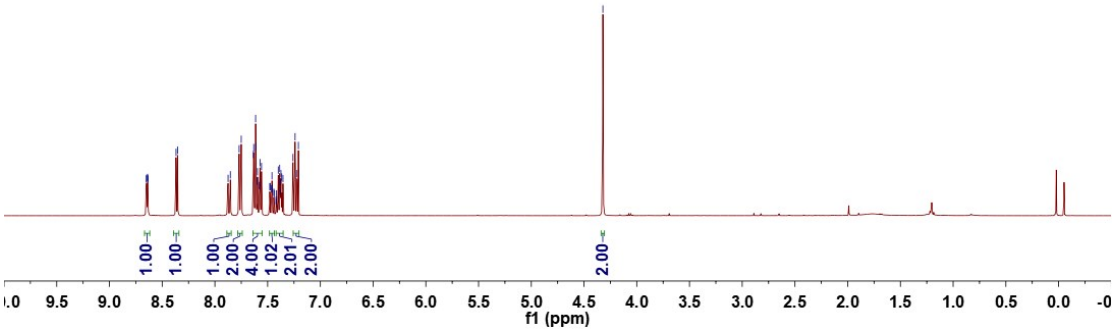
3fa

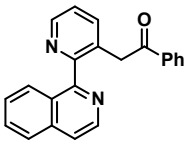
^{13}C NMR (100 MHz, $CDCl_3$)



3ga

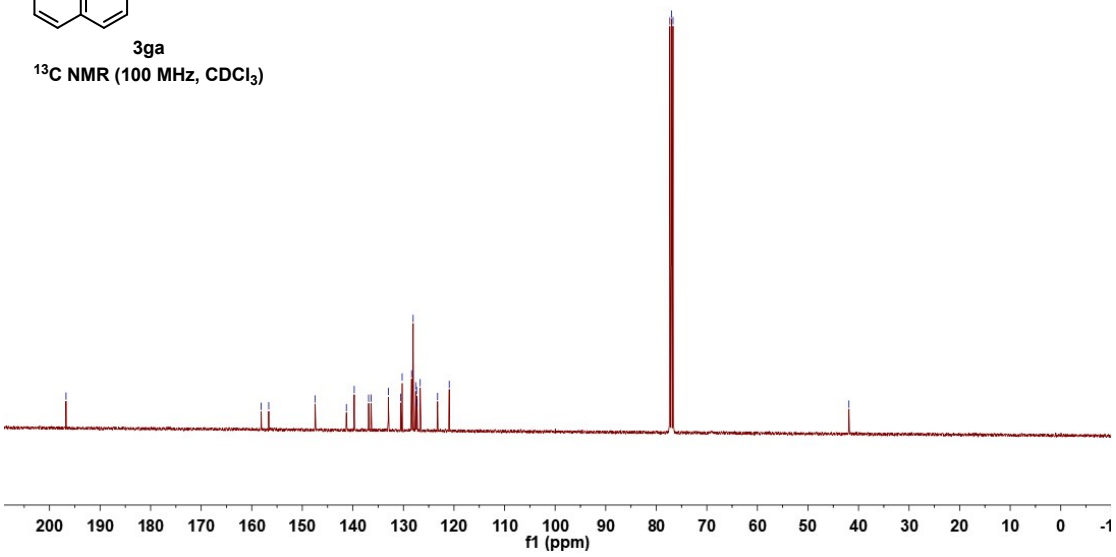
^{1}H NMR (400 MHz, $CDCl_3$)

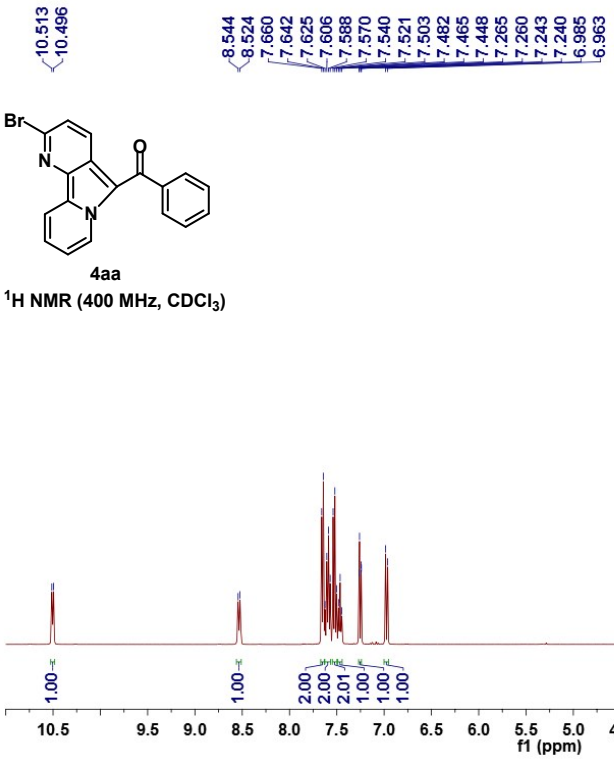




3ga

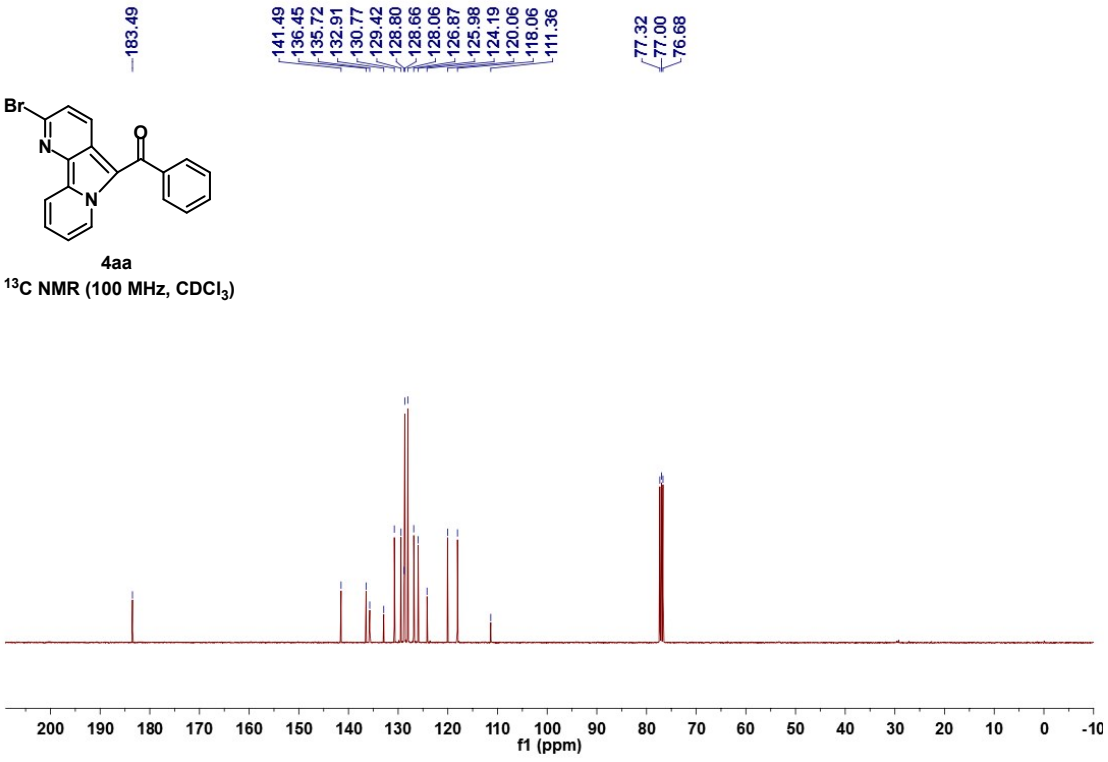
^{13}C NMR (100 MHz, $CDCl_3$)





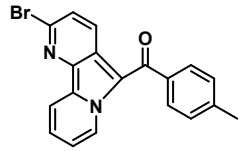
4aa

^{1}H NMR (400 MHz, $CDCl_3$)



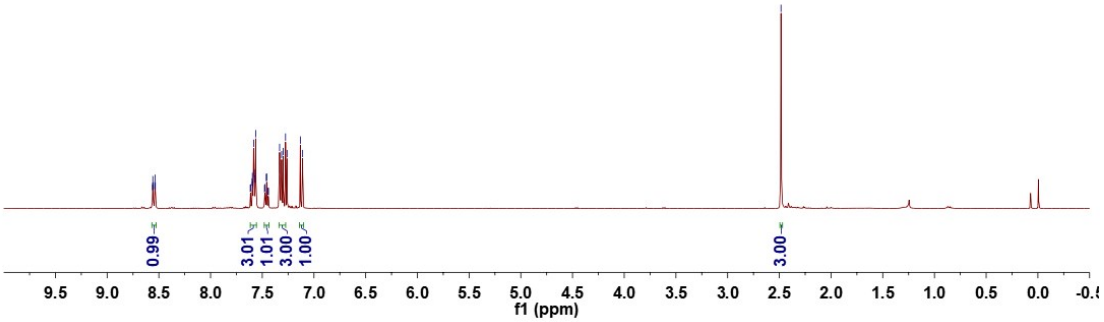
4aa

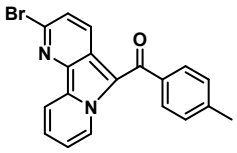
^{13}C NMR (100 MHz, $CDCl_3$)



4ab

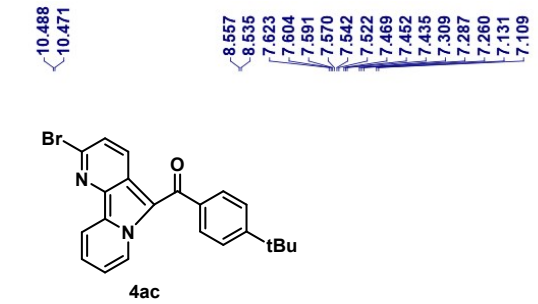
^{1}H NMR (400 MHz, $CDCl_3$)





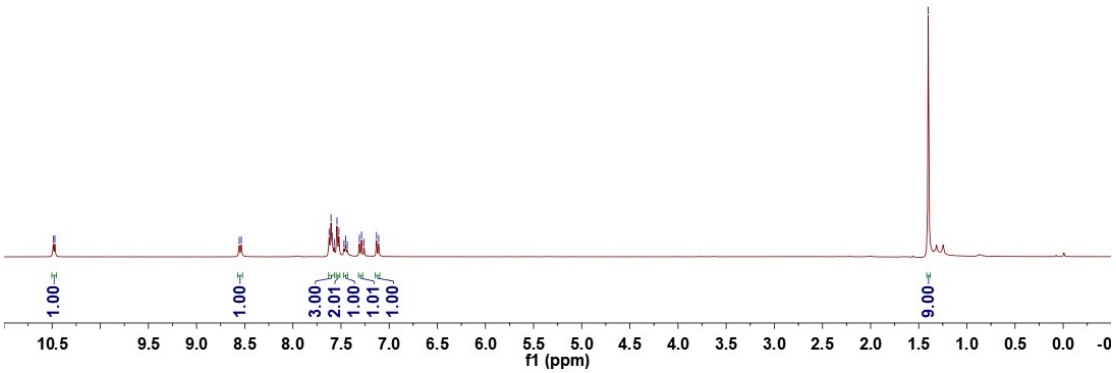
4ab

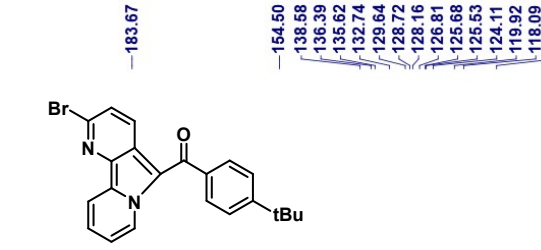
^{13}C NMR (100 MHz, $CDCl_3$)



4ac

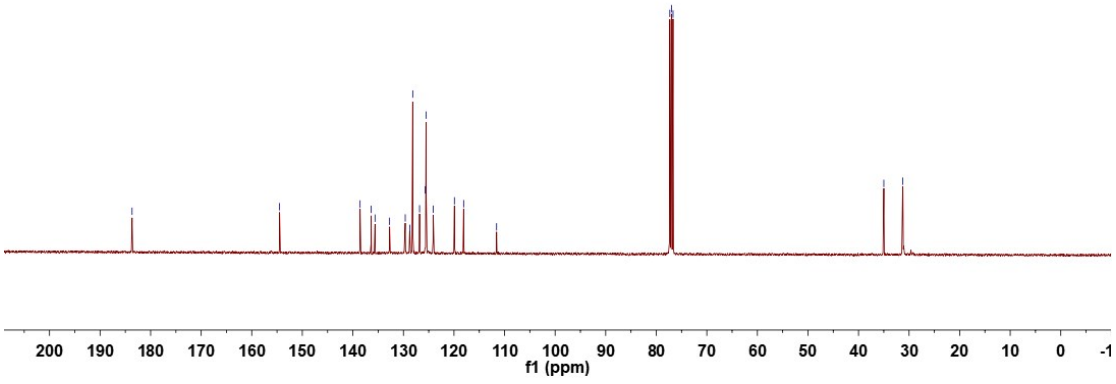
^{1}H NMR (400 MHz, $CDCl_3$)

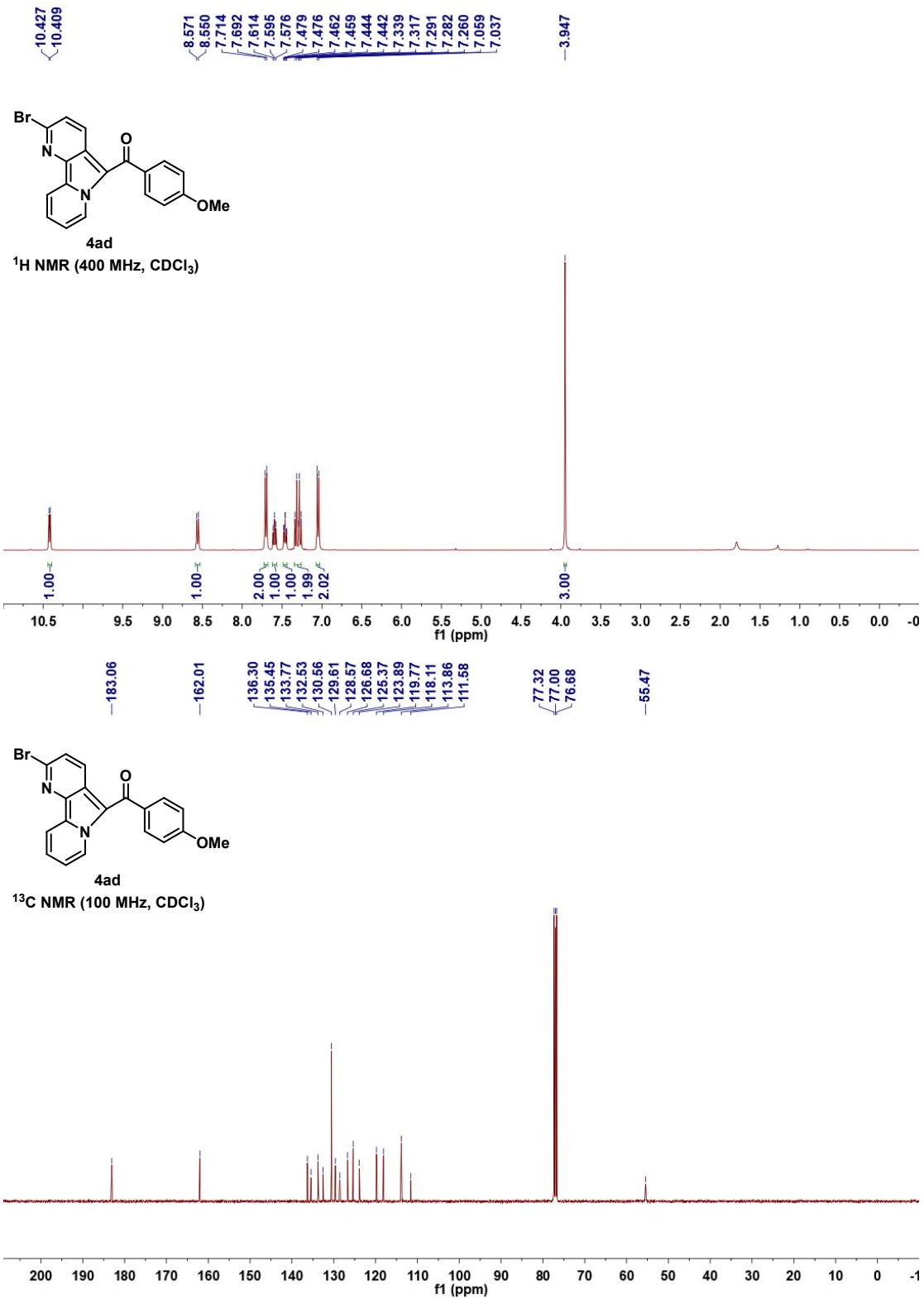


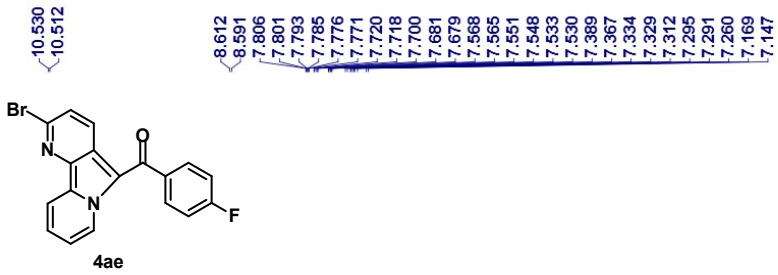


4ac

^{13}C NMR (100 MHz, $CDCl_3$)

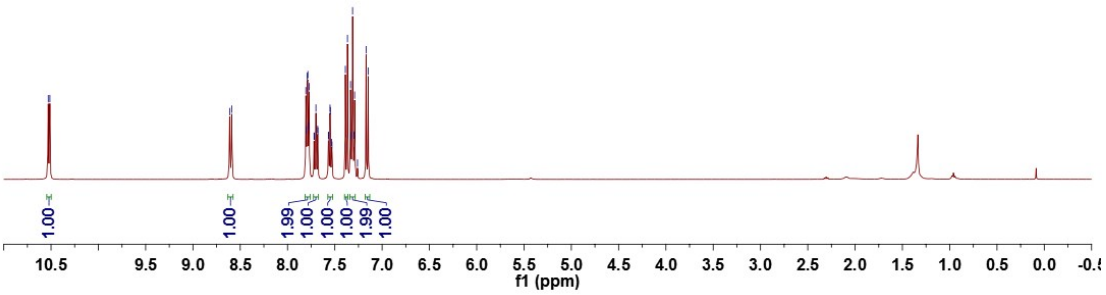


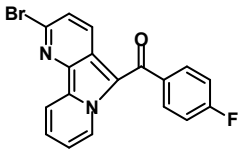

10.427
10.409
8.571
8.550
7.714
7.692
7.614
7.595
7.576
7.479
7.476
7.462
7.459
7.444
7.442
7.339
7.317
7.291
7.282
7.260
7.059
7.037
3.947
Br
N
O
N
OMe
4ad
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.00
1.00
1.00
1.99
2.02
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
183.06
162.01
136.30
135.45
133.77
132.53
130.56
129.61
128.57
126.68
125.37
123.89
119.77
118.11
113.86
111.58
77.32
77.00
76.68
55.47
Br
N
O
N
OMe
4ad
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4ae

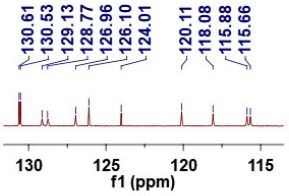
^{1}H NMR (400 MHz, $CDCl_3$)

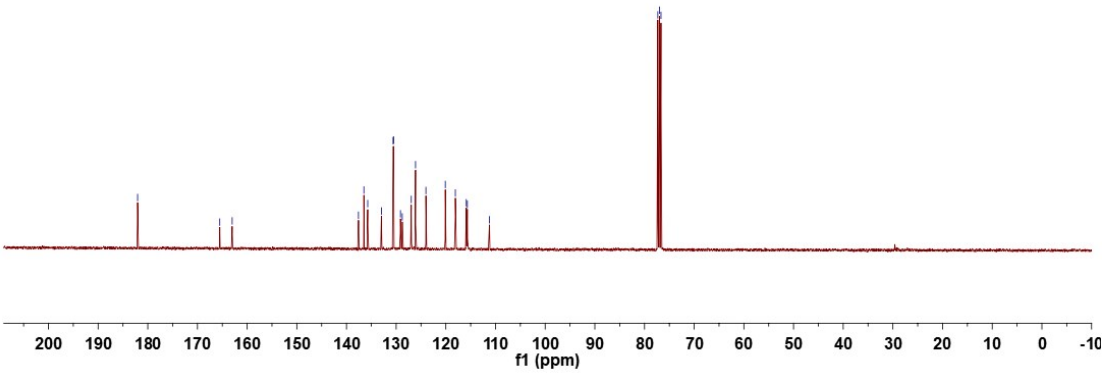


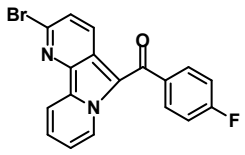


4ae

^{13}C NMR (100 MHz, $CDCl_3$)

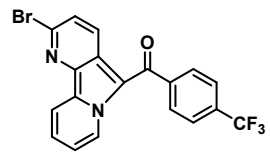






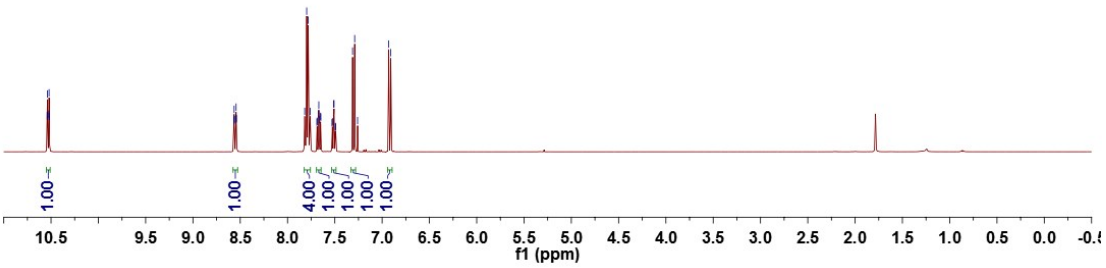
4ae

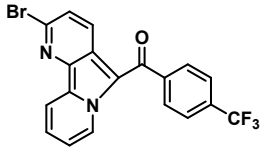
^{19}F NMR (376 MHz, $CDCl_3$)



4ag

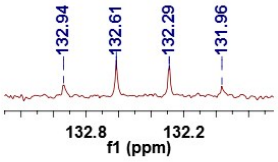
^{1}H NMR (400 MHz, $CDCl_3$)

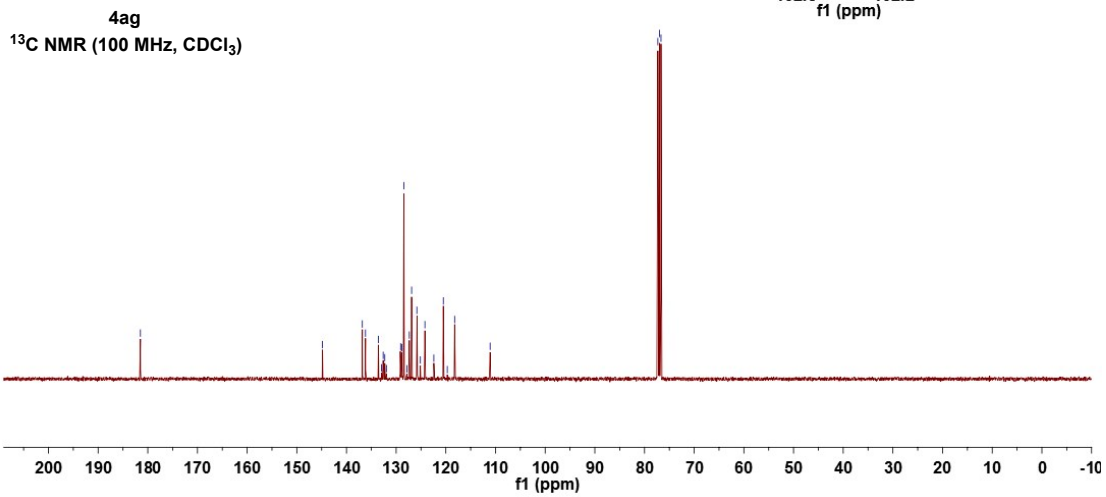


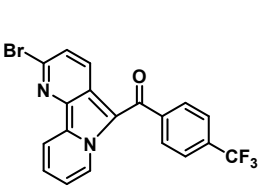


4ag

^{13}C NMR (100 MHz, $CDCl_3$)

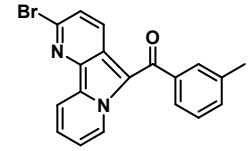






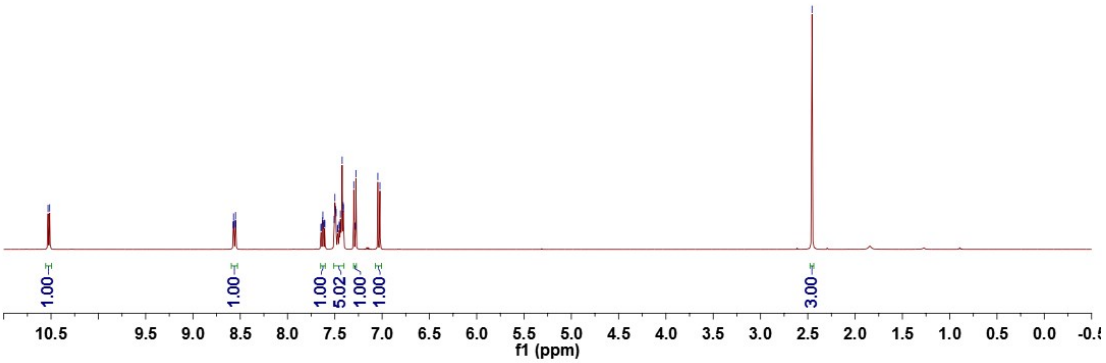
4ag

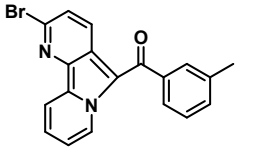
^{19}F NMR (376 MHz, $CDCl_3$)



4ai

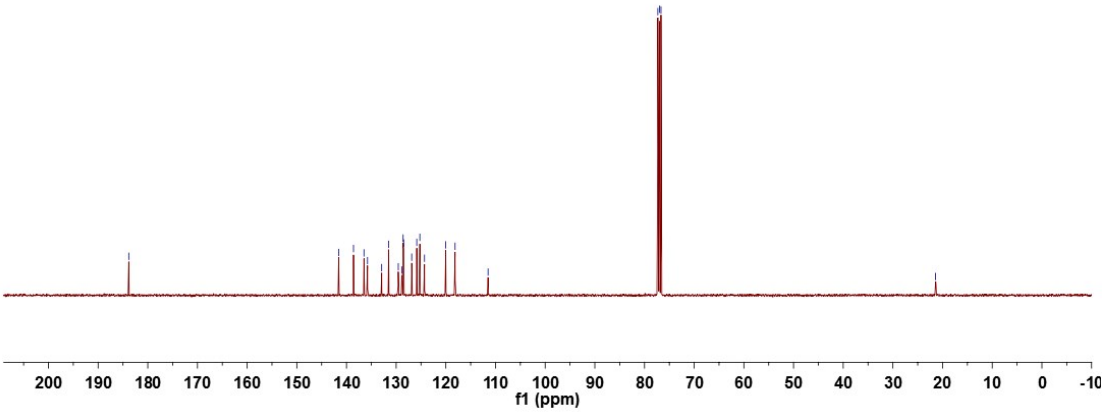
^{1}H NMR (400 MHz, $CDCl_3$)

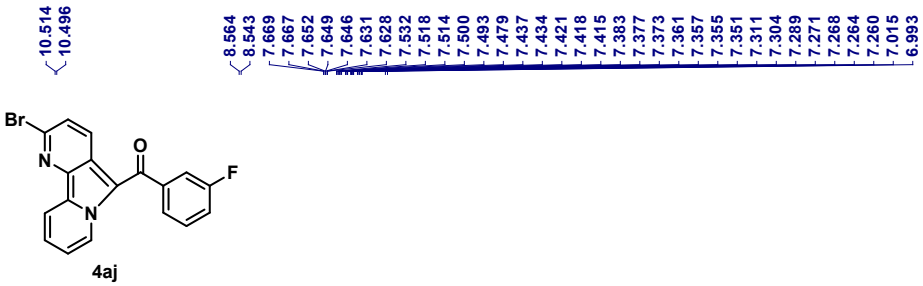




4ai

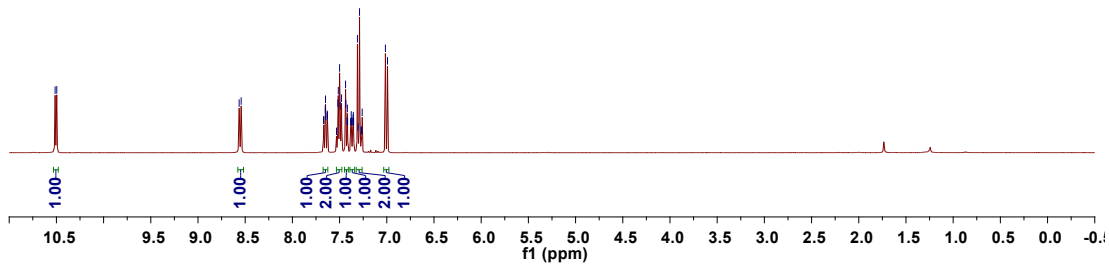
^{13}C NMR (100 MHz, $CDCl_3$)

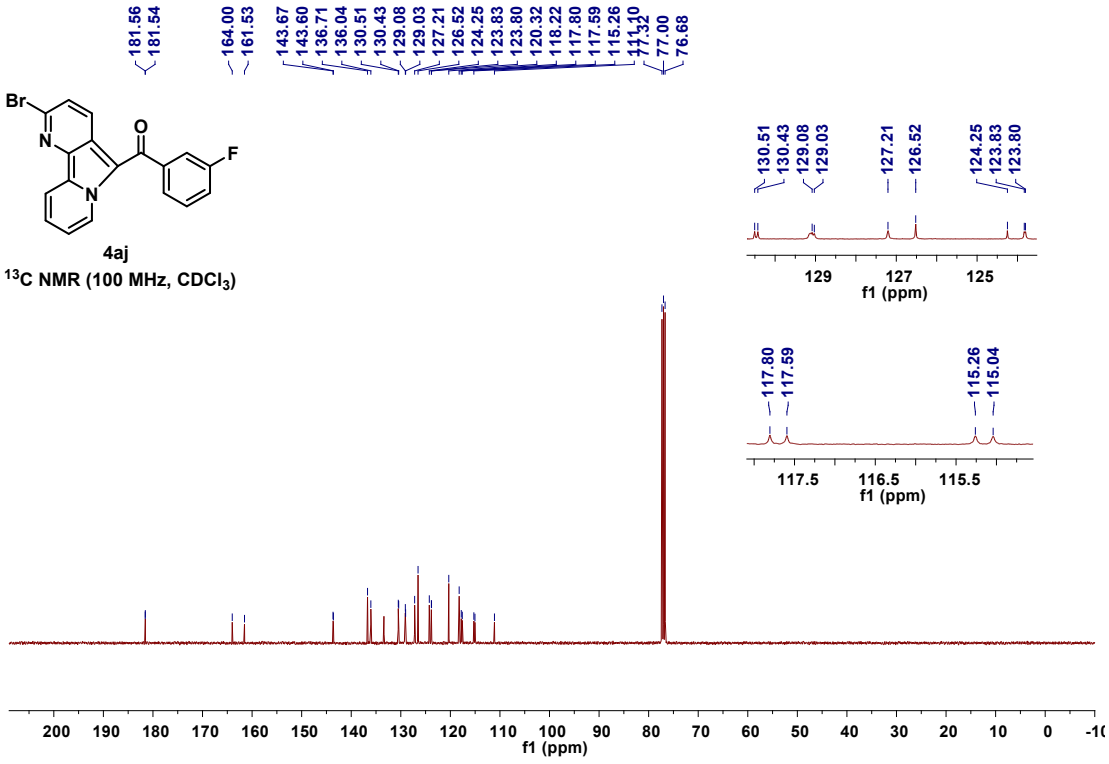




4aj

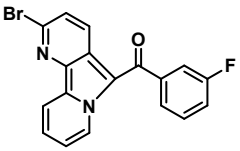
^{1}H NMR (400 MHz, $CDCl_3$)





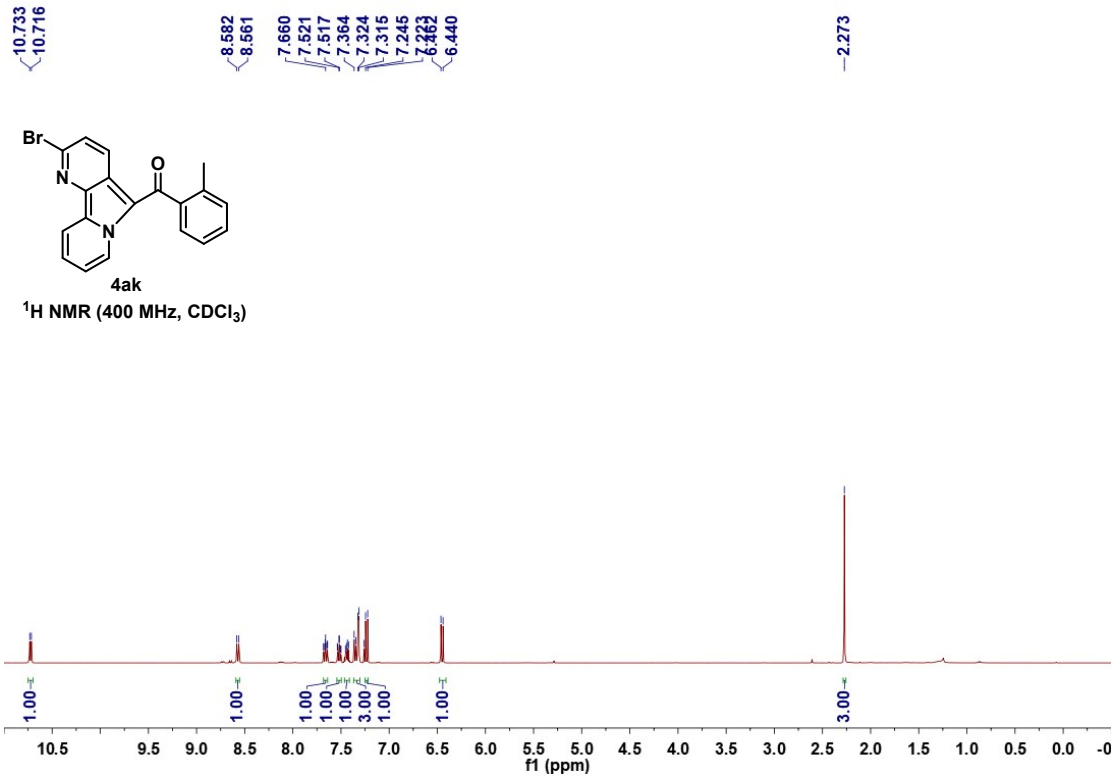
4aj

^{13}C NMR (100 MHz, $CDCl_3$)



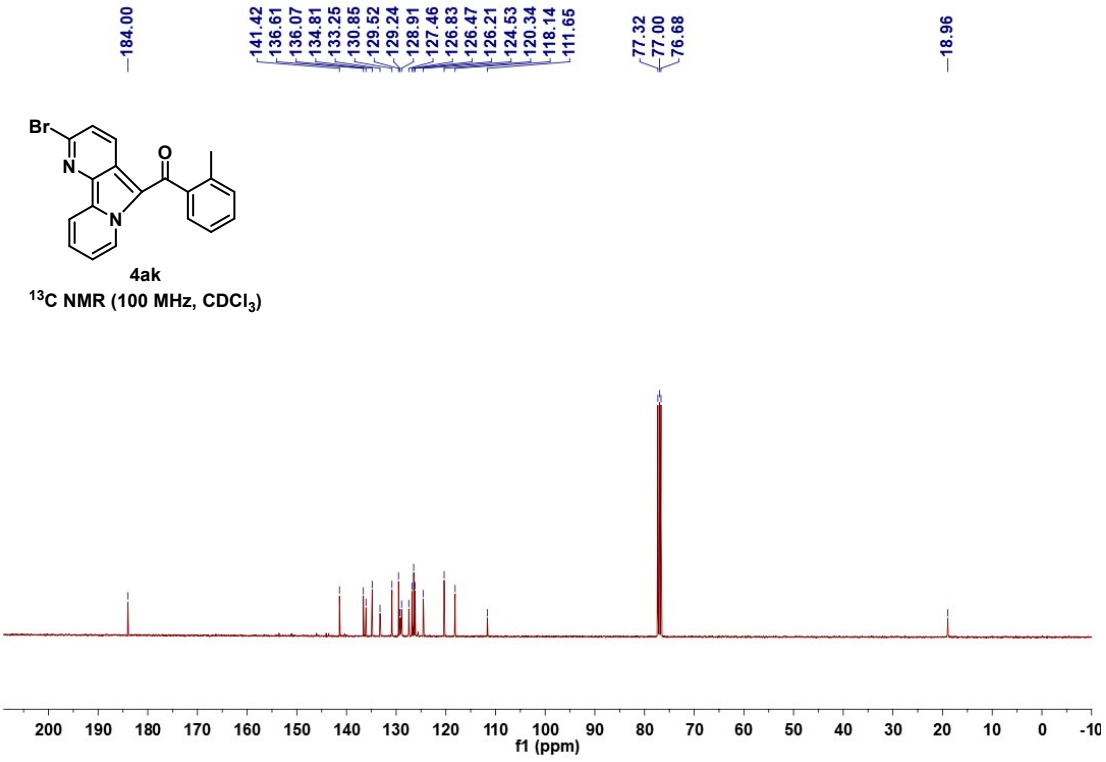
4aj

^{19}F NMR (376 MHz, $CDCl_3$)



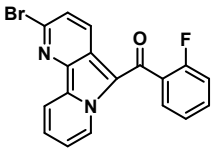
4ak

^{1}H NMR (400 MHz, $CDCl_3$)



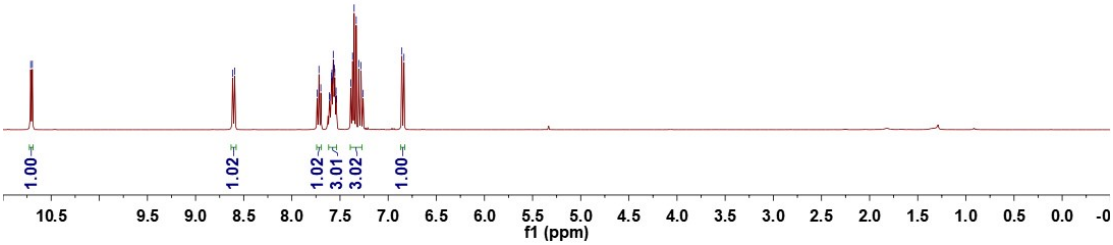
4ak

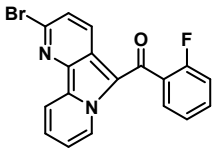
^{13}C NMR (100 MHz, $CDCl_3$)



4al

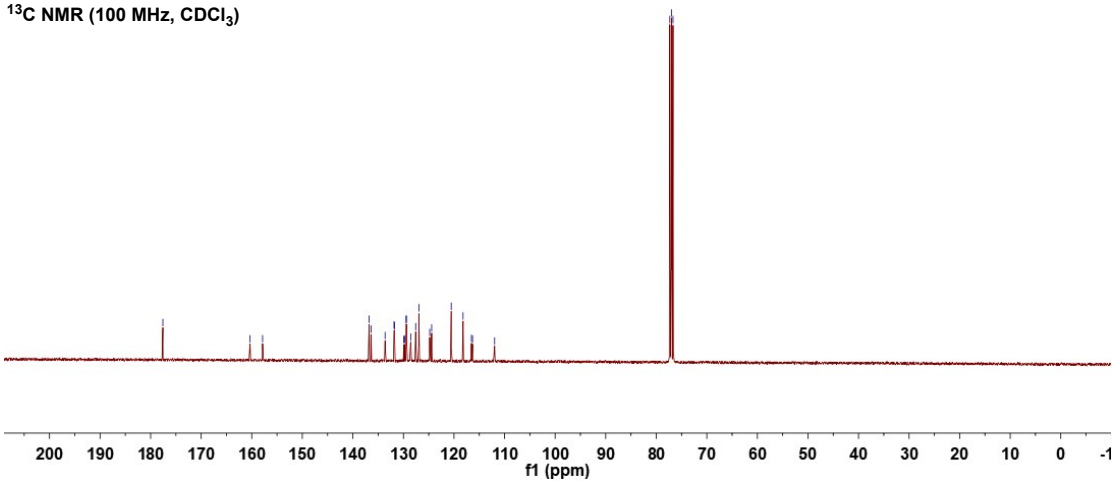
^{1}H NMR (400 MHz, $CDCl_3$)

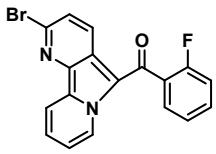




4al

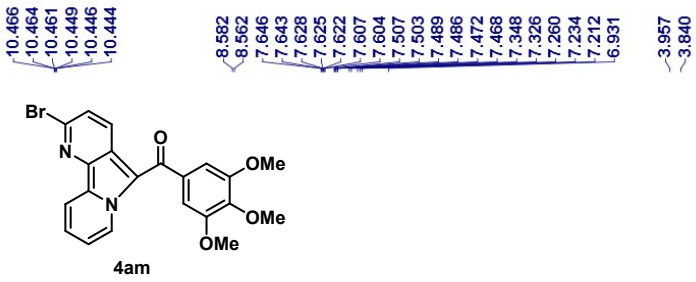
^{13}C NMR (100 MHz, $CDCl_3$)





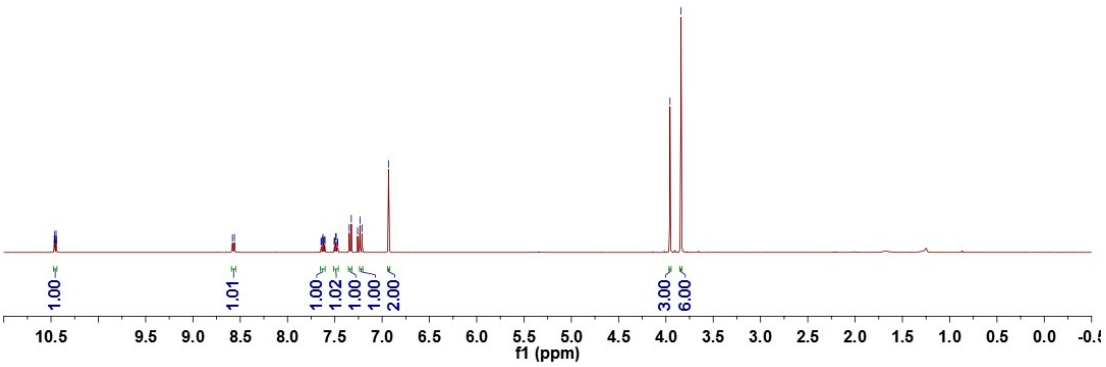
4al

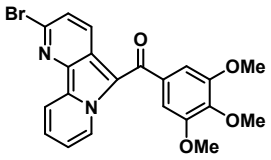
^{19}F NMR (376 MHz, $CDCl_3$)



4am

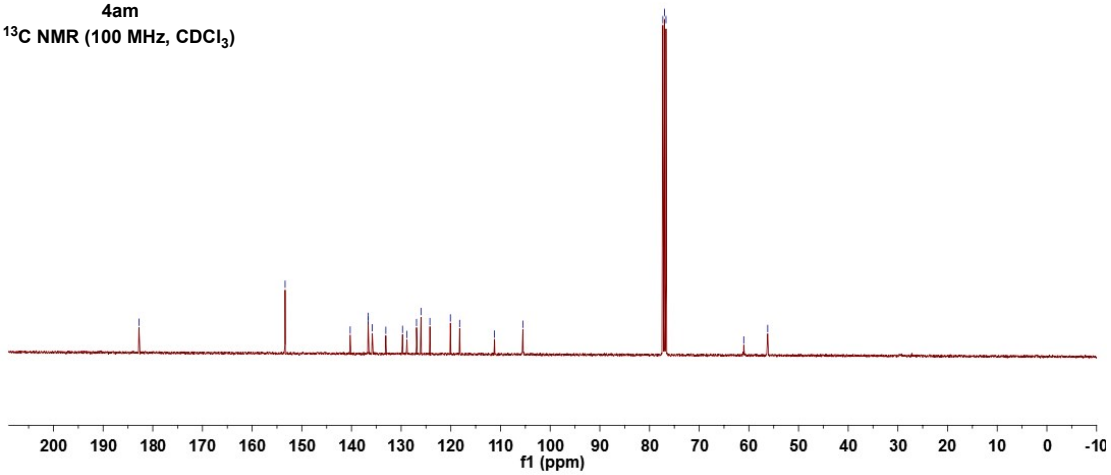
^{1}H NMR (400 MHz, $CDCl_3$)

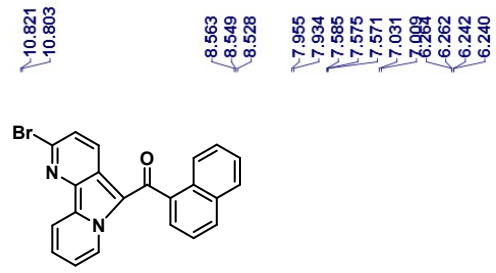




4am

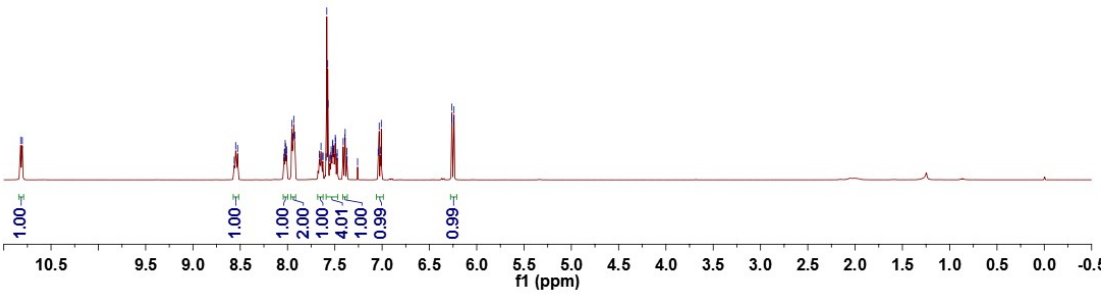
^{13}C NMR (100 MHz, $CDCl_3$)

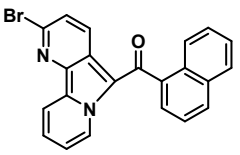




4an

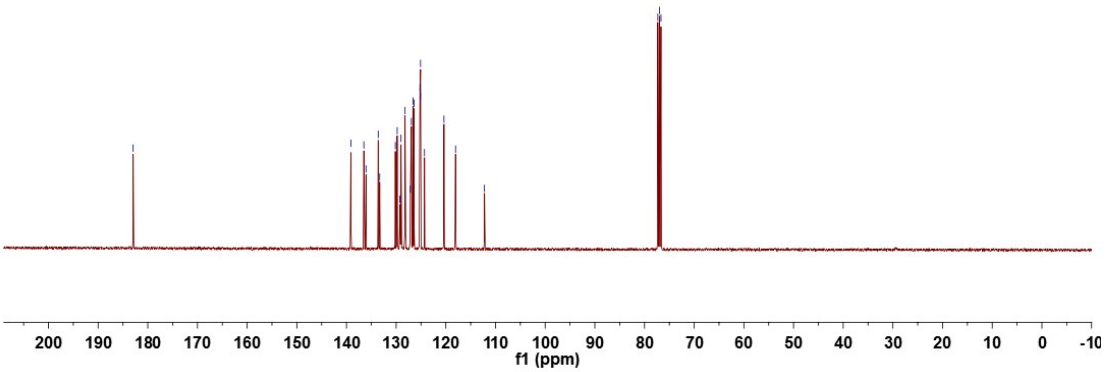
^{1}H NMR (400 MHz, $CDCl_3$)

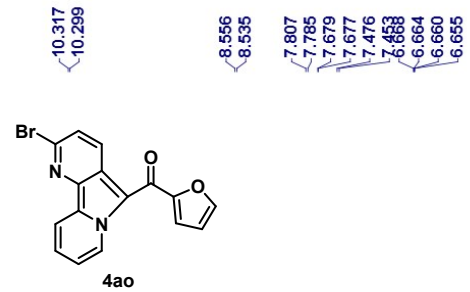




4an

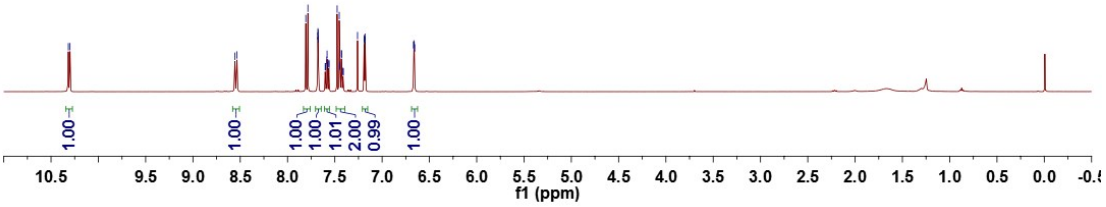
^{13}C NMR (100 MHz, $CDCl_3$)

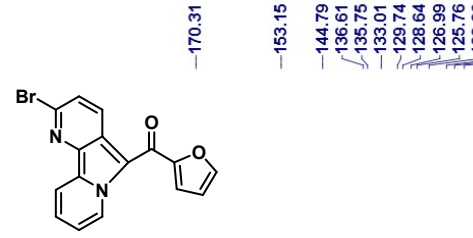




4ao

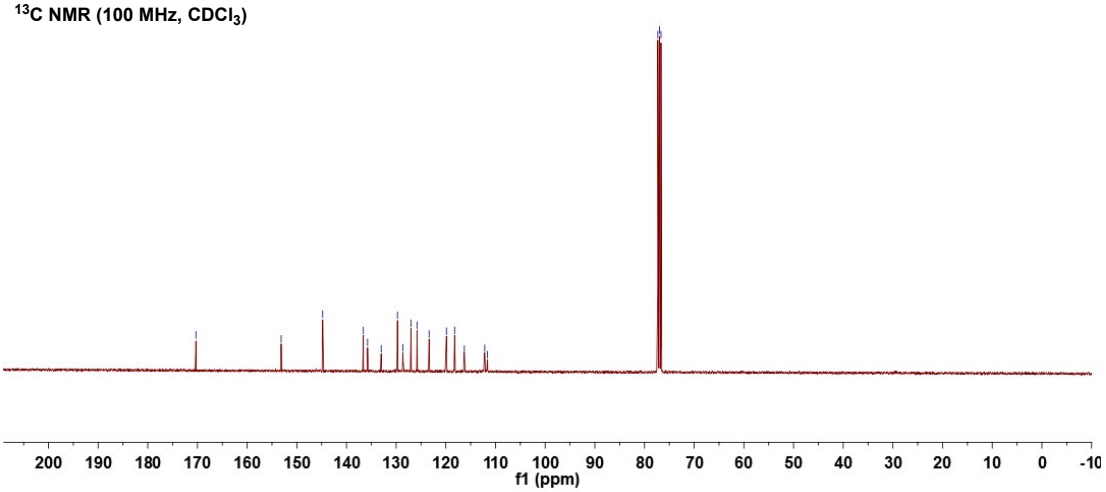
^{1}H NMR (400 MHz, $CDCl_3$)

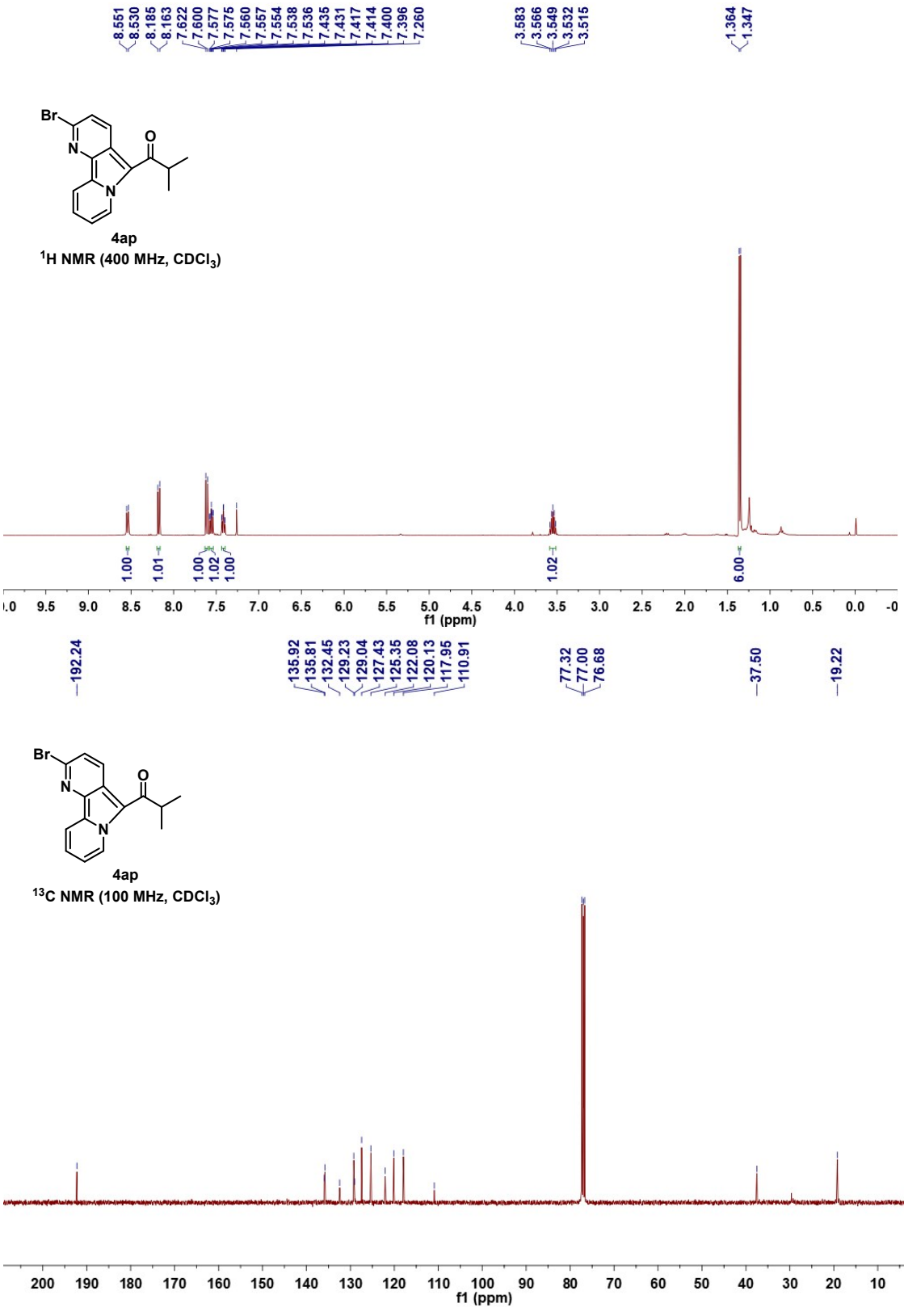




4ao

^{13}C NMR (100 MHz, $CDCl_3$)

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8.163
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7.600
7.577
7.575
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7.557
7.554
7.538
7.536
7.435
7.431
7.417
7.414
7.400
7.396
7.260
3.583
3.566
3.549
3.532
3.515
1.364
1.347
Br
N
O
N
4ap
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.00
1.02
1.00
1.02
6.00
f1 (ppm)
192.24
135.92
135.81
132.45
129.23
129.04
127.43
125.35
122.08
120.13
117.95
110.91
77.32
77.00
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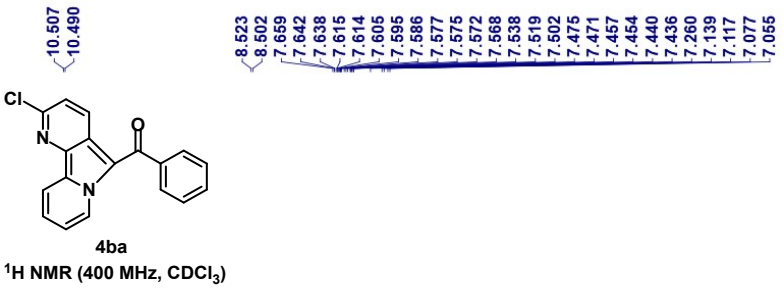
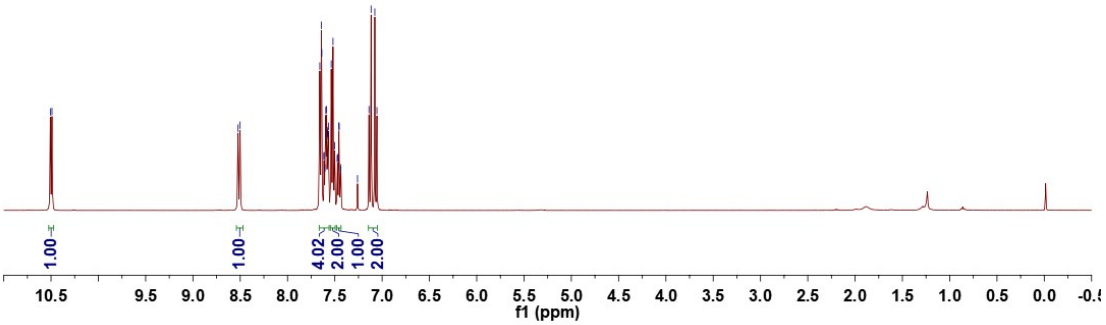
37.50
19.22
Br
N
O
N
4ap
13C NMR (100 MHz, CDCl3)
f1 (ppm)



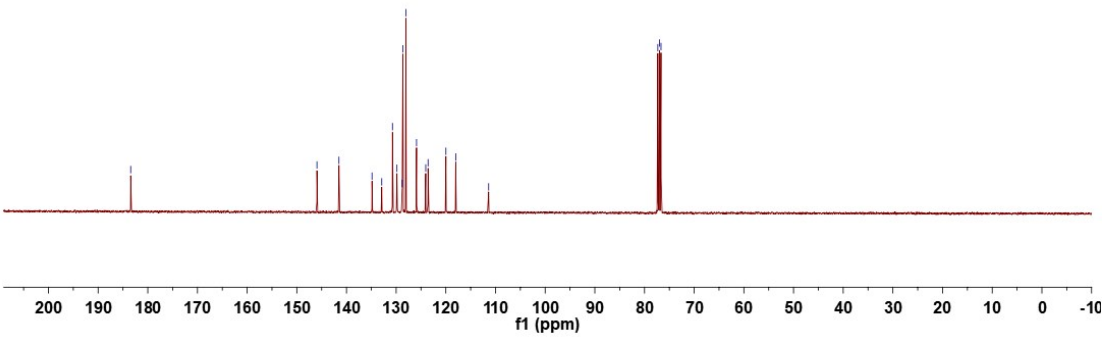
4ba

^{1}H NMR (400 MHz, $CDCl_3$)



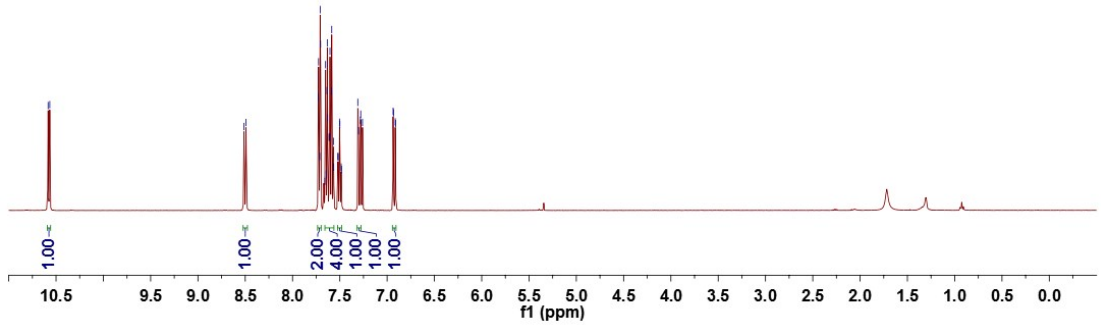
4ba

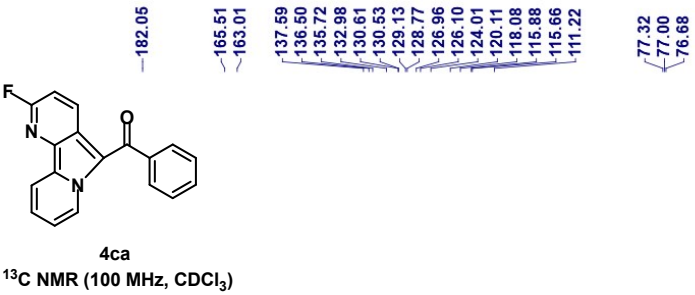
^{13}C NMR (100 MHz, $CDCl_3$)



4ca

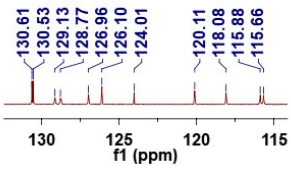
^{1}H NMR (400 MHz, $CDCl_3$)

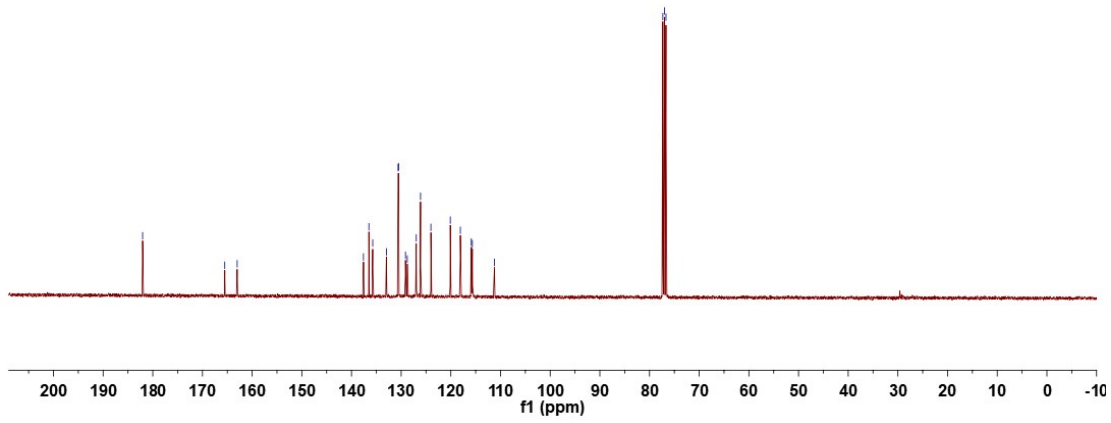


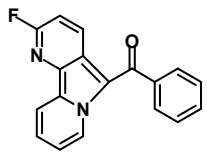


4ca

^{13}C NMR (100 MHz, $CDCl_3$)

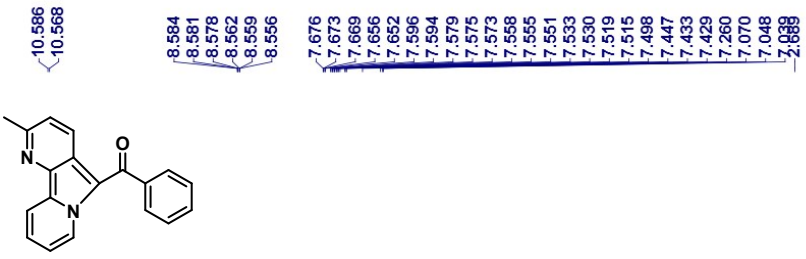






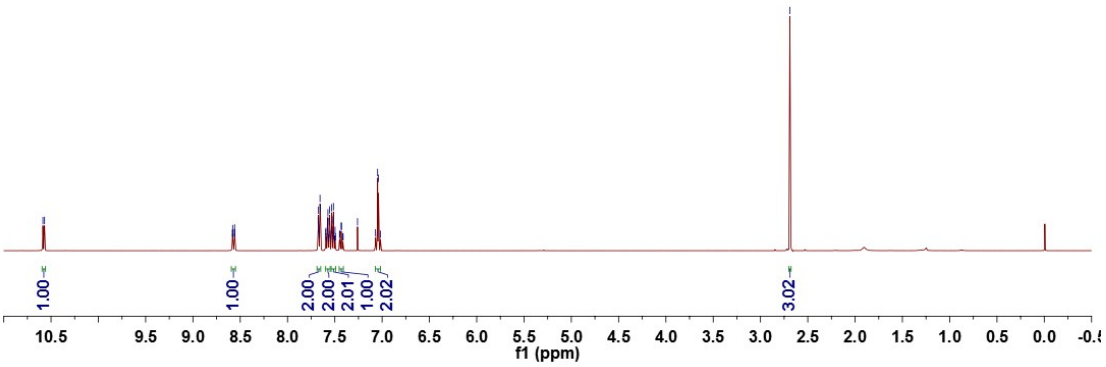
4ca

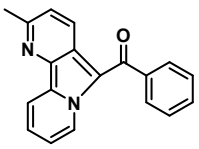
^{19}F NMR (376 MHz, $CDCl_3$)



4da

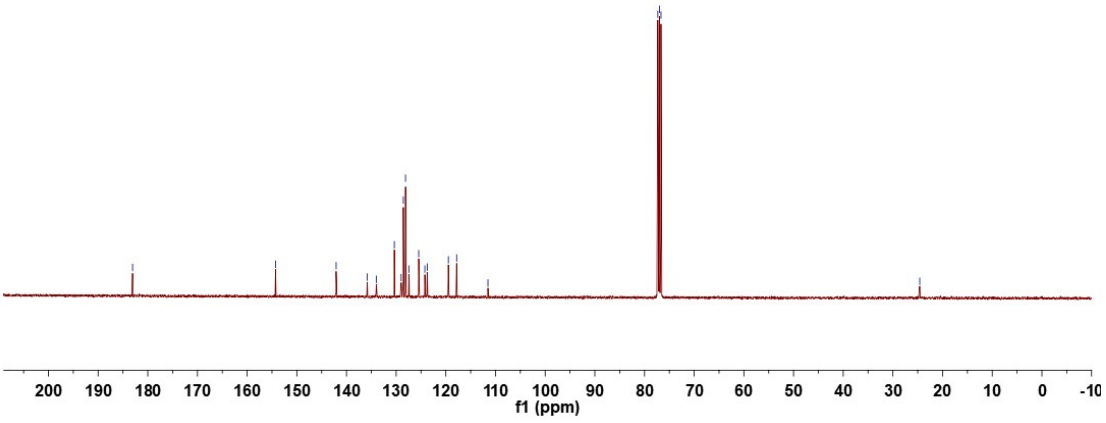
^{1}H NMR (400 MHz, $CDCl_3$)

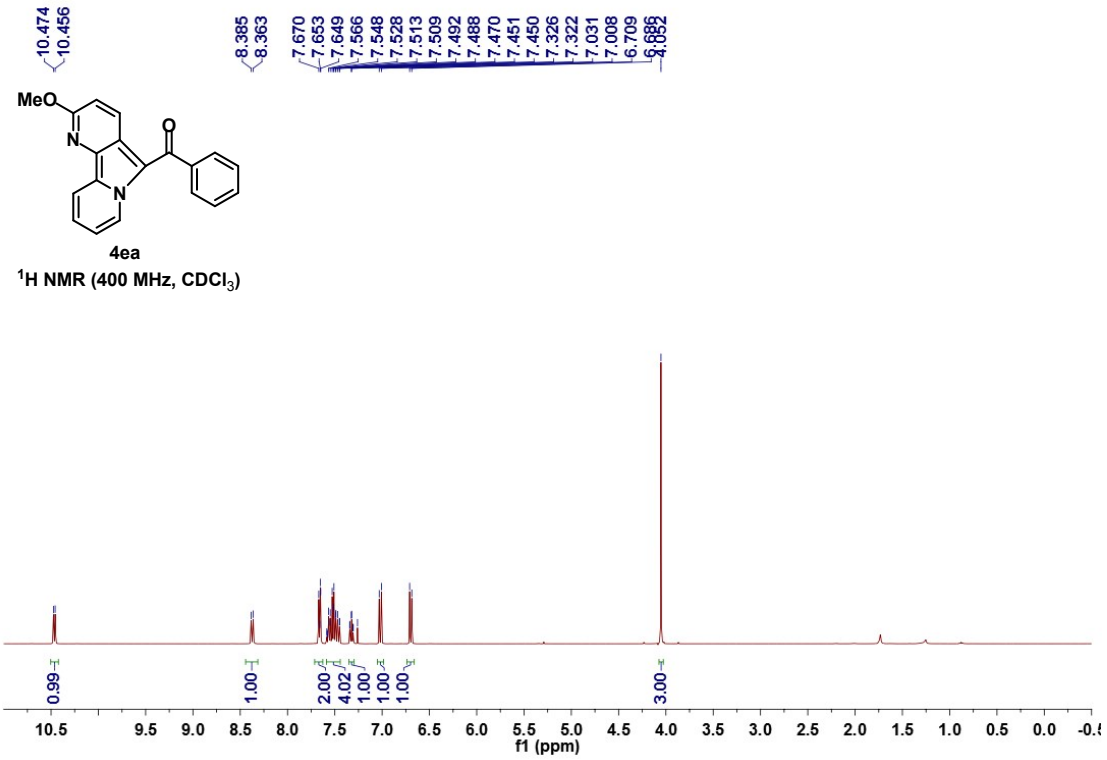




4da

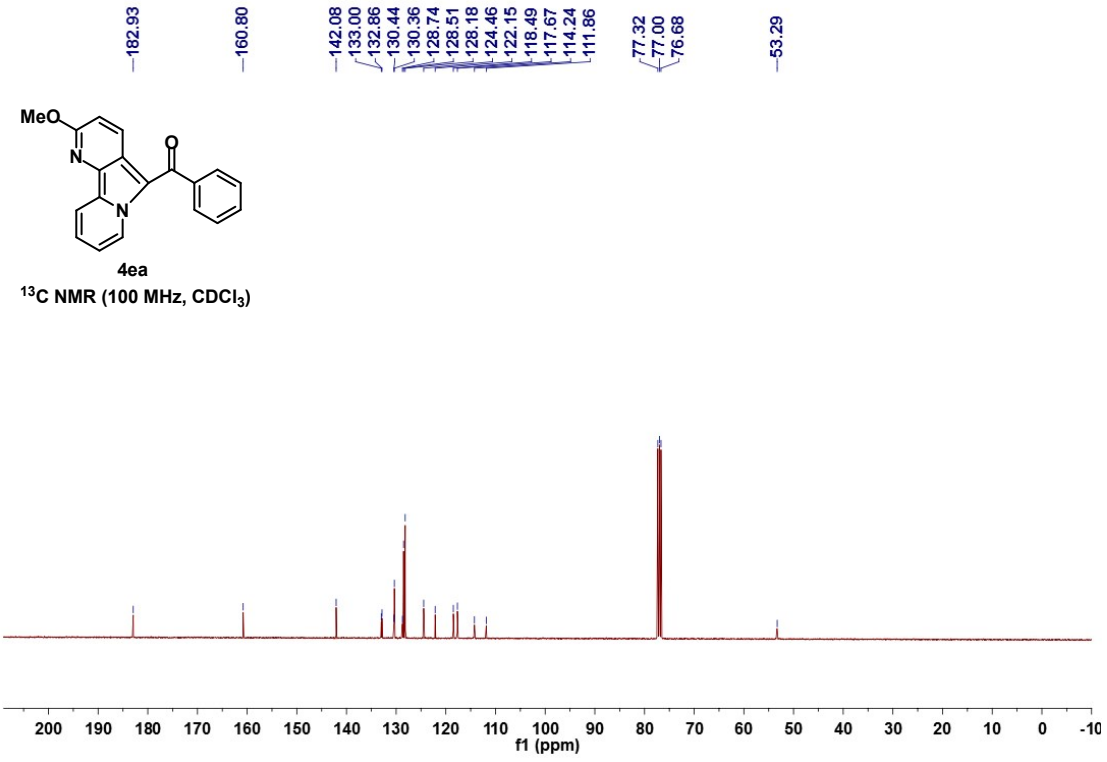
^{13}C NMR (100 MHz, $CDCl_3$)





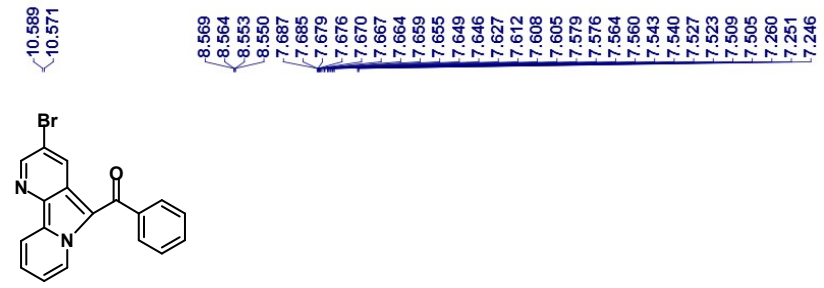
4ea

^{1}H NMR (400 MHz, $CDCl_3$)



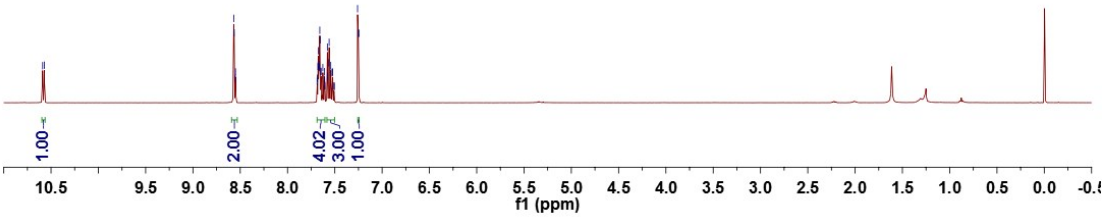
4ea

^{13}C NMR (100 MHz, $CDCl_3$)



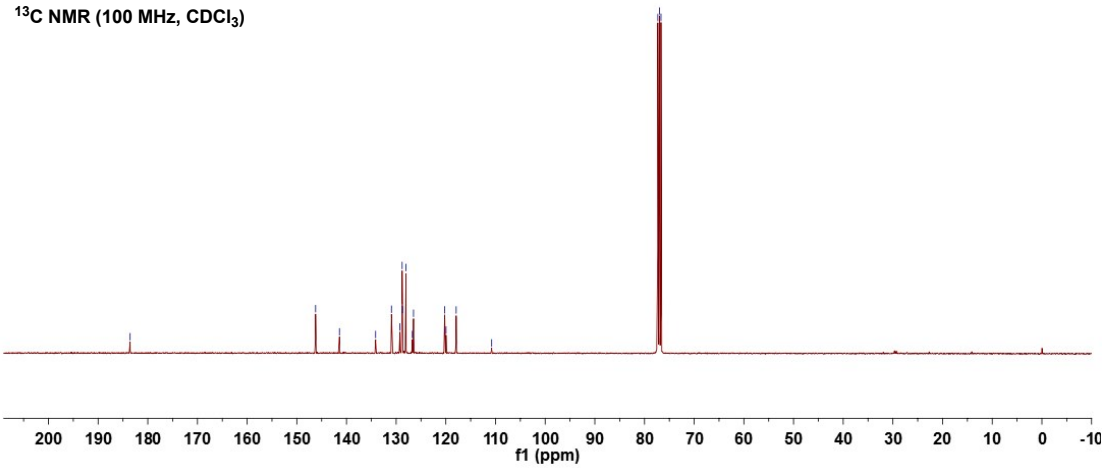
4fa

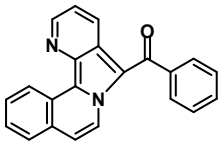
^{1}H NMR (400 MHz, $CDCl_3$)



4fa

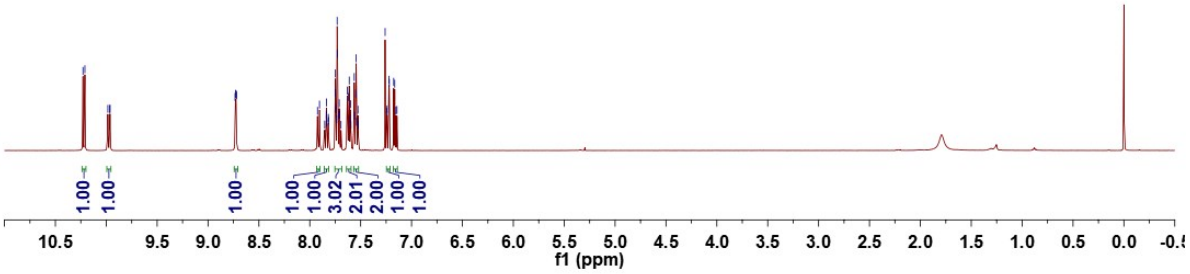
^{13}C NMR (100 MHz, $CDCl_3$)

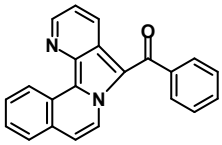




4ga

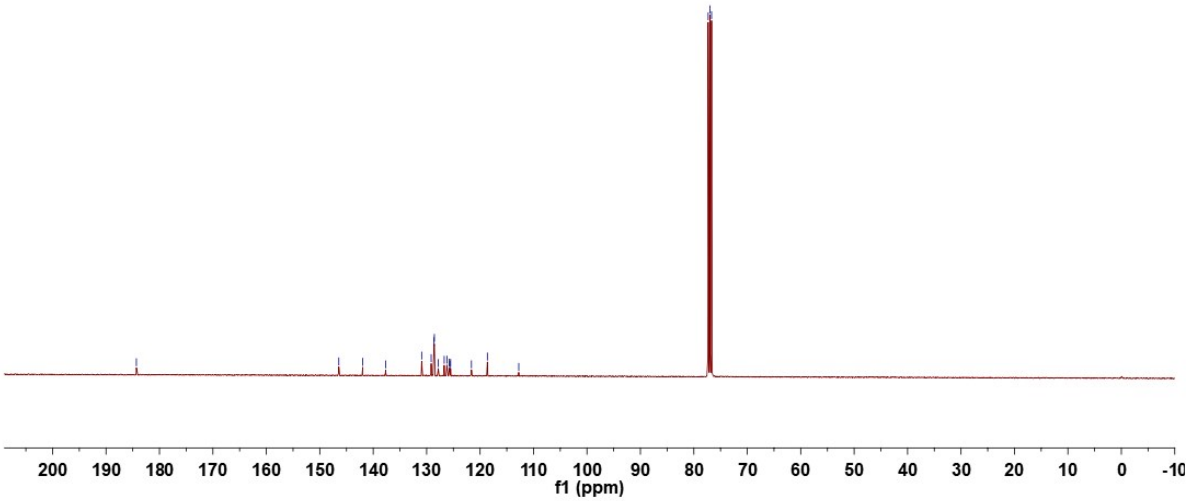
^{1}H NMR (400 MHz, $CDCl_3$)

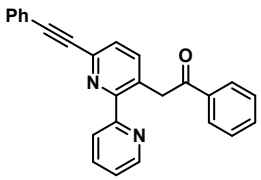




4ga

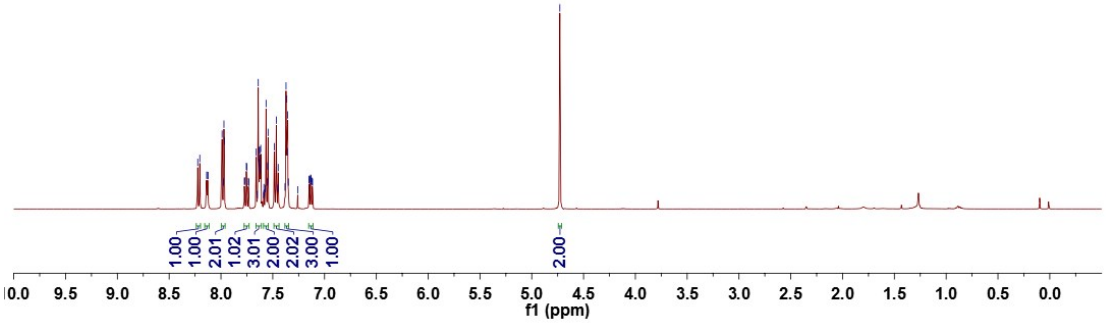
^{13}C NMR (100 MHz, $CDCl_3$)

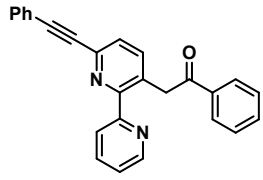




5

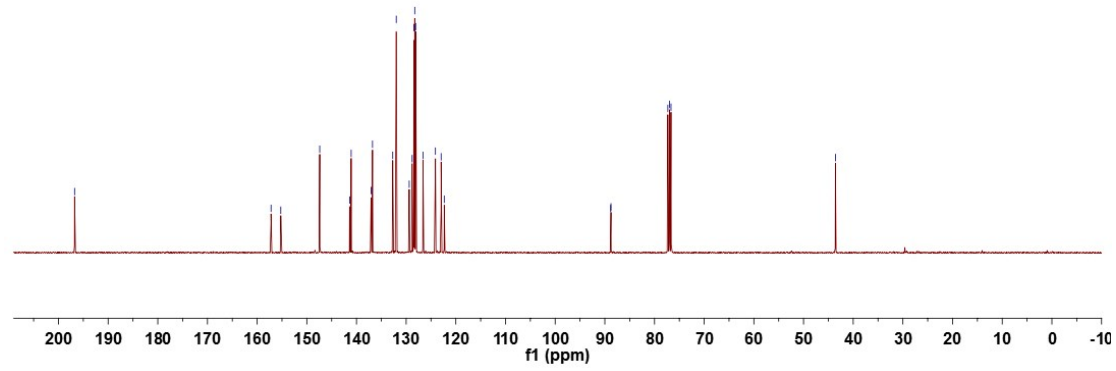
^{1}H NMR (400 MHz, $CDCl_3$)

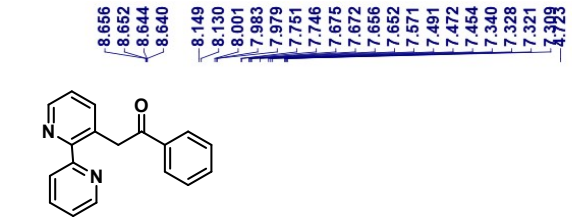




5

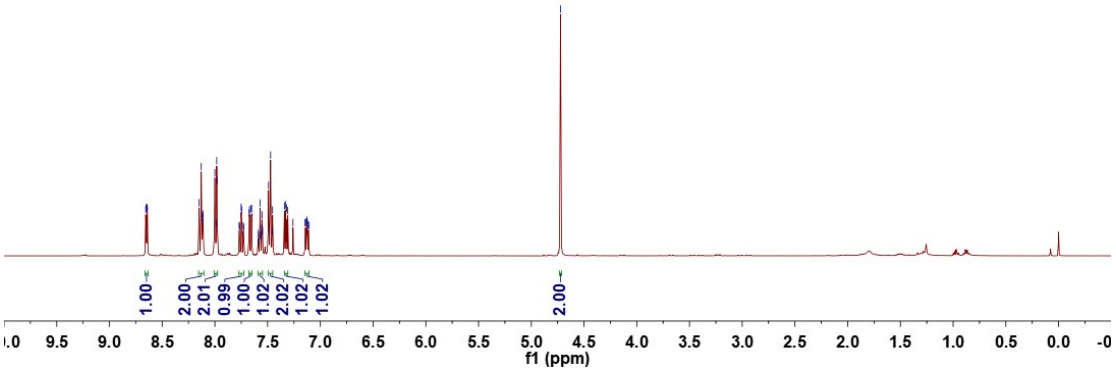
^{13}C NMR (100 MHz, $CDCl_3$)

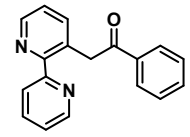




6

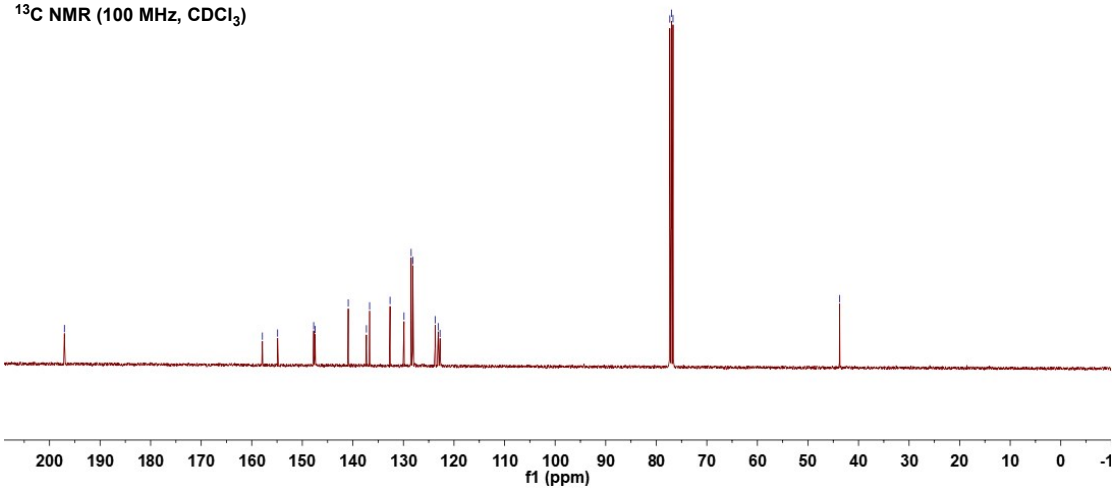
^{1}H NMR (400 MHz, $CDCl_3$)

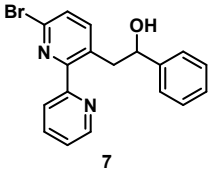




6

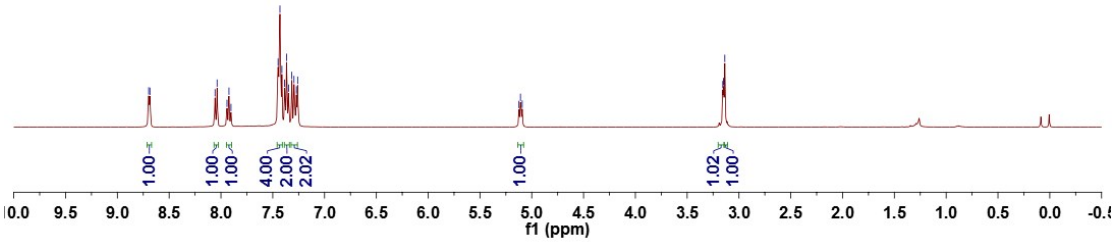
^{13}C NMR (100 MHz, $CDCl_3$)

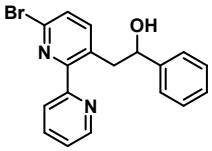




7

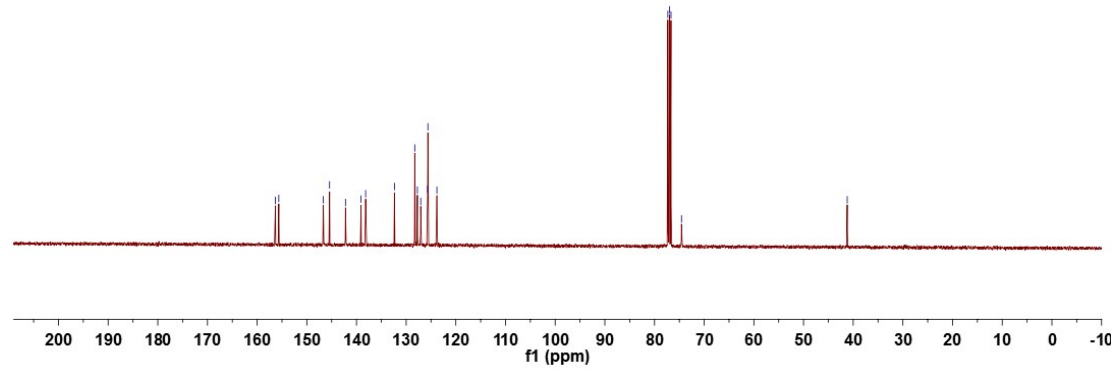
^{1}H NMR (400 MHz, $CDCl_3$)

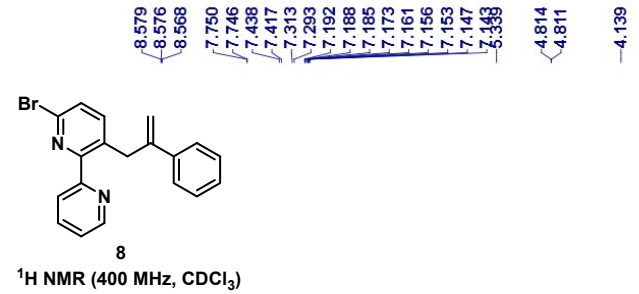




7

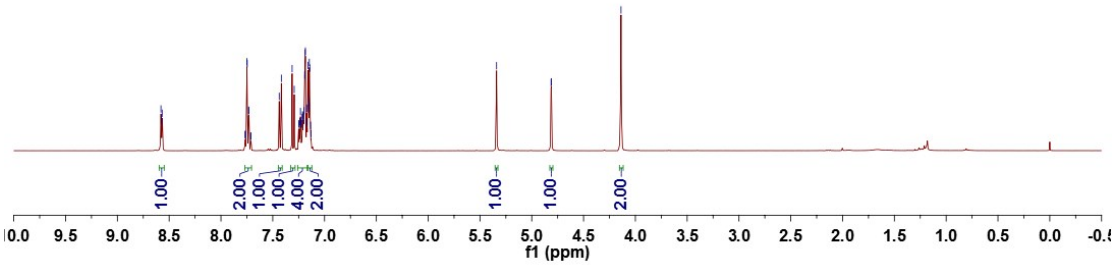
^{13}C NMR (100 MHz, $CDCl_3$)

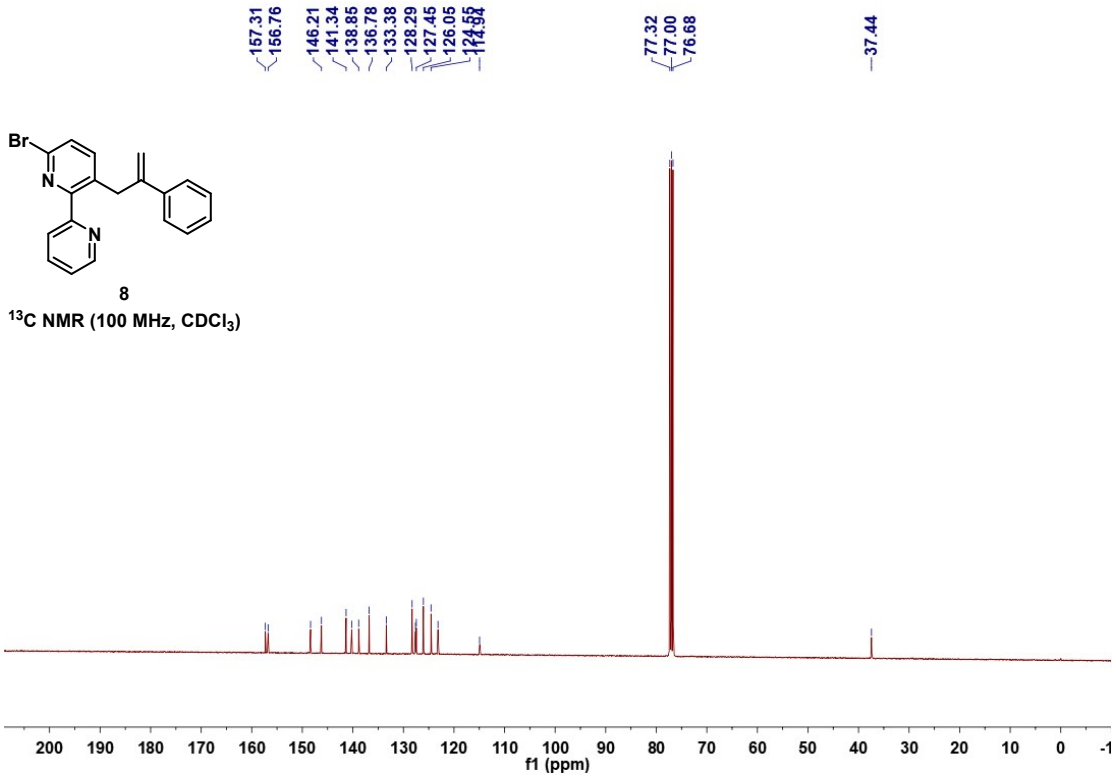




8

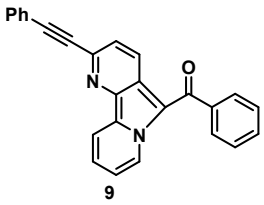
^{1}H NMR (400 MHz, $CDCl_3$)





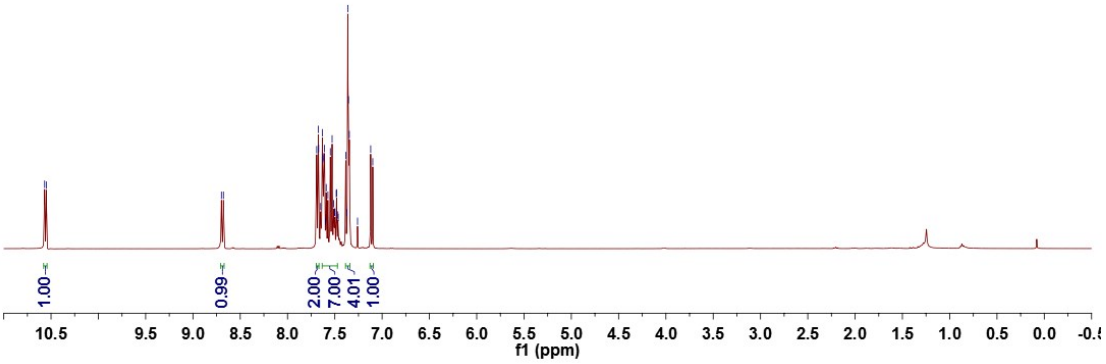
8

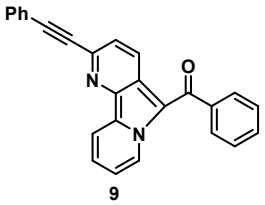
^{13}C NMR (100 MHz, $CDCl_3$)



9

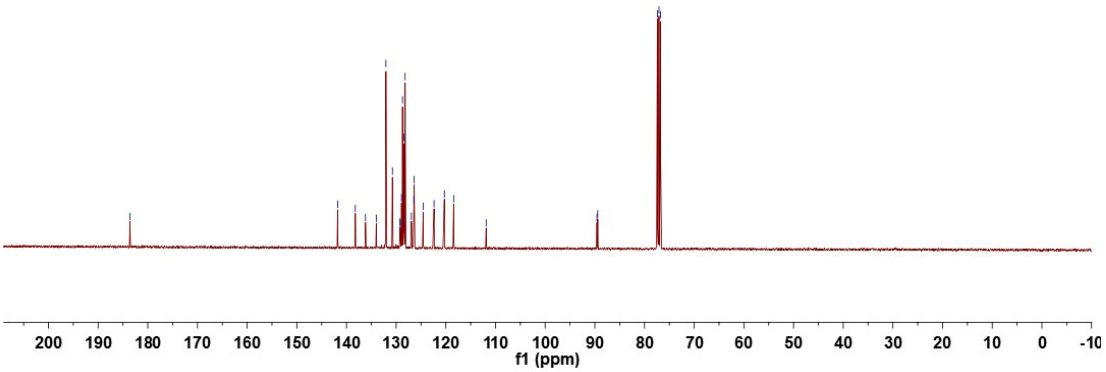
^{1}H NMR (400 MHz, $CDCl_3$)

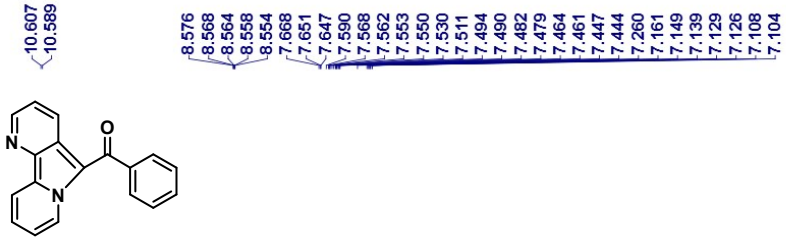




9

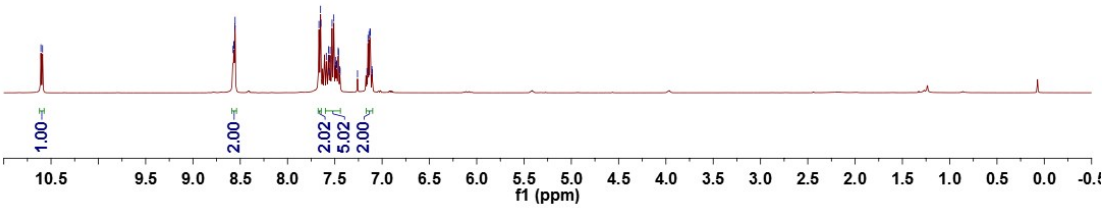
^{13}C NMR (100 MHz, $CDCl_3$)





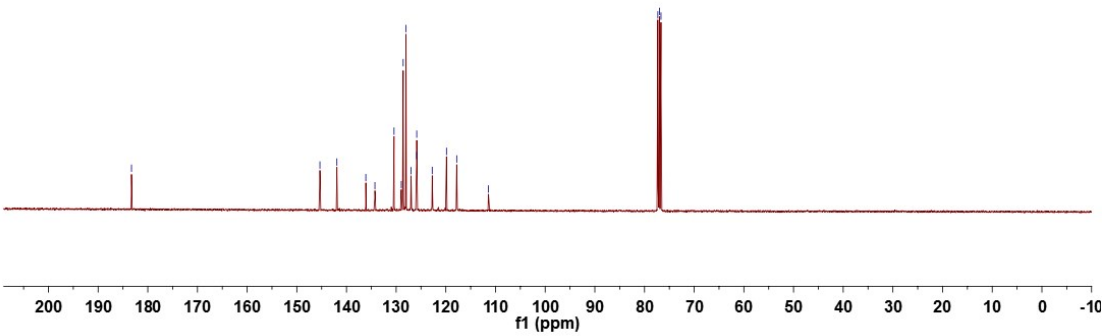
10

^{1}H NMR (400 MHz, $CDCl_3$)



10

^{13}C NMR (100 MHz, $CDCl_3$)



Crystallography:

Single crystals of complexes **3ab** (CCDC reference number 2033676), **3ea** (CCDC reference number 2034526) and **4aa** (CCDC reference number 2034525) suitable for X-ray diffraction were obtained by crystallization from n-hexane/CH_2Cl_2 (2:1). Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation (ω−2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for these complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Tables 1-14.

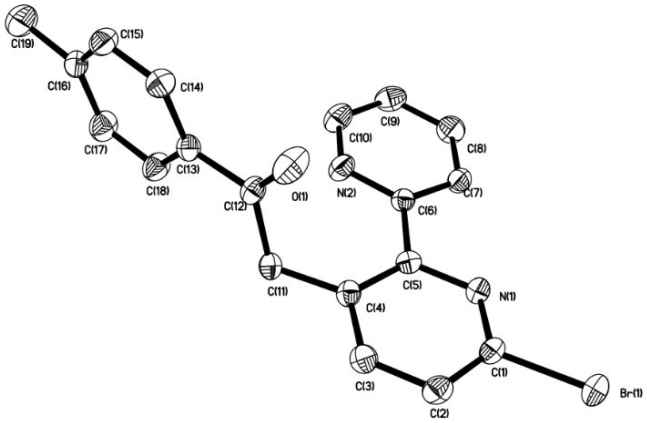


Figure 1. ORTEP drawing for the product **3ab**.

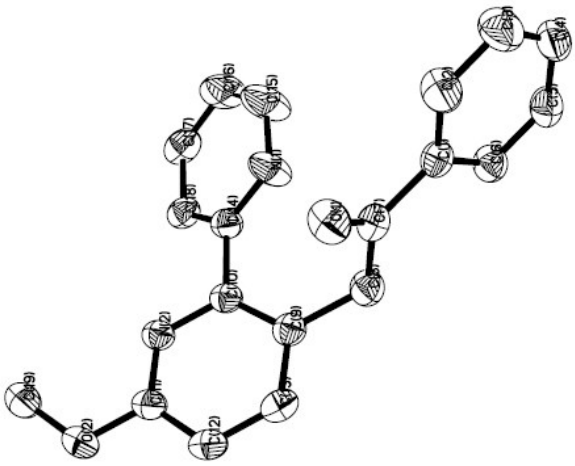


Figure 2. ORTEP drawing for the product **3ea**.

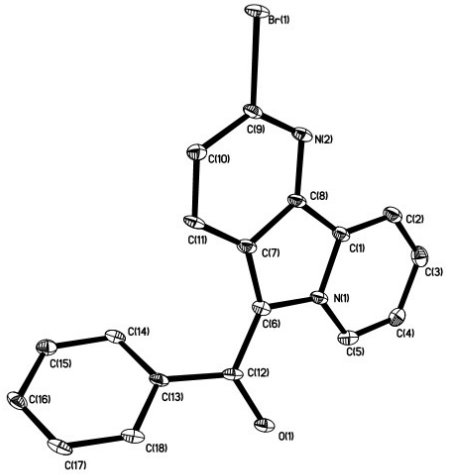


Figure 3. ORTEP drawing for the product **4aa**.

X-Ray Crystallographic Data of 3ab, 3ea and 4aa:

X-Ray crystallographic data of **3ab**:

Table 1. Crystal data and structure refinement for N191217A.

Identification code	n191217a
Empirical formula	C19 H15 Br N2 O
Formula weight	367.24
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.730(4) A alpha = 90 deg.
	b = 9.218(3) A beta = 95.635(7) deg.
	c = 16.091(6) A gamma = 90 deg.
Volume	1583.9(10) A^3
Z, Calculated density	4, 1.540 Mg/m^3
Absorption coefficient	2.601 mm^-1
F(000)	744
Crystal size	0.220 x 0.210 x 0.180 mm
Theta range for data collection	1.907 to 26.499 deg.
Limiting indices	-13<=h<=13, -9<=k<=11, -20<=l<=18
Reflections collected / unique	10044 / 3285 [R(int) = 0.0611]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3285 / 0 / 208
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0416, wR2 = 0.0812
R indices (all data)	R1 = 0.0737, wR2 = 0.0885
Extinction coefficient	n/a
Largest diff. peak and hole	0.337 and -0.433 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for N191217A. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	6298(1)	5282(1)	2119(1)	46(1)
N(1)	4741(2)	5400(3)	3364(2)	35(1)
N(2)	2626(2)	5526(3)	4947(2)	44(1)
O(1)	2653(2)	8942(3)	4460(2)	61(1)
C(1)	5677(3)	6092(3)	3081(2)	34(1)
C(2)	6232(3)	7317(3)	3439(2)	42(1)
C(3)	5760(3)	7817(3)	4142(2)	40(1)
C(4)	4760(3)	7143(3)	4477(2)	33(1)
C(5)	4264(2)	5921(3)	4054(2)	32(1)
C(6)	3205(3)	5041(3)	4313(2)	33(1)
C(7)	2850(3)	3766(3)	3900(2)	43(1)
C(8)	1884(3)	2956(4)	4168(2)	53(1)
C(9)	1291(3)	3460(4)	4822(2)	53(1)
C(10)	1692(3)	4731(4)	5193(2)	53(1)
C(11)	4314(3)	7745(3)	5254(2)	38(1)
C(12)	3043(3)	8460(3)	5135(2)	35(1)
C(13)	2327(3)	8660(3)	5870(2)	34(1)
C(14)	1302(3)	9578(3)	5797(2)	42(1)
C(15)	582(3)	9766(4)	6446(2)	49(1)
C(16)	849(3)	9054(4)	7196(2)	47(1)
C(17)	1889(3)	8176(4)	7269(2)	53(1)
C(18)	2620(3)	7979(4)	6626(2)	48(1)
C(19)	40(3)	9216(5)	7891(2)	73(1)

Table 3. Bond lengths [A] and angles [deg] for N191217A.

Br(1)-C(1)	1.899(3)
N(1)-C(1)	1.309(4)
N(1)-C(5)	1.355(4)
N(2)-C(6)	1.324(4)
N(2)-C(10)	1.333(4)
O(1)-C(12)	1.210(3)
C(1)-C(2)	1.376(4)
C(2)-C(3)	1.365(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.393(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.394(4)
C(4)-C(11)	1.489(4)
C(5)-C(6)	1.489(4)
C(6)-C(7)	1.385(4)
C(7)-C(8)	1.381(4)
C(7)-H(7)	0.9300
C(8)-C(9)	1.364(5)
C(8)-H(8)	0.9300
C(9)-C(10)	1.365(5)
C(9)-H(9)	0.9300
C(10)-H(10)	0.9300
C(11)-C(12)	1.509(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.483(4)
C(13)-C(18)	1.378(4)
C(13)-C(14)	1.384(4)
C(14)-C(15)	1.369(5)
C(14)-H(14)	0.9300
C(15)-C(16)	1.379(5)
C(15)-H(15)	0.9300
C(16)-C(17)	1.374(5)
C(16)-C(19)	1.489(5)
C(17)-C(18)	1.370(4)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-H(19A)	0.9600
C(19)-H(19B)	0.9600
C(19)-H(19C)	0.9600
C(1)-N(1)-C(5)	118.4(3)
C(6)-N(2)-C(10)	117.8(3)

N(1)-C(1)-C(2)	124.8(3)
N(1)-C(1)-Br(1)	115.8(2)
C(2)-C(1)-Br(1)	119.4(2)
C(3)-C(2)-C(1)	116.3(3)
C(3)-C(2)-H(2)	121.8
C(1)-C(2)-H(2)	121.8
C(2)-C(3)-C(4)	122.2(3)
C(2)-C(3)-H(3)	118.9
C(4)-C(3)-H(3)	118.9
C(5)-C(4)-C(3)	116.3(3)
C(5)-C(4)-C(11)	124.9(3)
C(3)-C(4)-C(11)	118.8(3)
N(1)-C(5)-C(4)	122.0(3)
N(1)-C(5)-C(6)	113.3(2)
C(4)-C(5)-C(6)	124.7(3)
N(2)-C(6)-C(7)	121.9(3)
N(2)-C(6)-C(5)	117.4(3)
C(7)-C(6)-C(5)	120.6(3)
C(8)-C(7)-C(6)	119.3(3)
C(8)-C(7)-H(7)	120.4
C(6)-C(7)-H(7)	120.4
C(9)-C(8)-C(7)	118.5(3)
C(9)-C(8)-H(8)	120.7
C(7)-C(8)-H(8)	120.7
C(8)-C(9)-C(10)	118.6(3)
C(8)-C(9)-H(9)	120.7
C(10)-C(9)-H(9)	120.7
N(2)-C(10)-C(9)	123.8(3)
N(2)-C(10)-H(10)	118.1
C(9)-C(10)-H(10)	118.1
C(4)-C(11)-C(12)	114.7(2)
C(4)-C(11)-H(11A)	108.6
C(12)-C(11)-H(11A)	108.6
C(4)-C(11)-H(11B)	108.6
C(12)-C(11)-H(11B)	108.6
H(11A)-C(11)-H(11B)	107.6
O(1)-C(12)-C(13)	120.7(3)
O(1)-C(12)-C(11)	120.1(3)
C(13)-C(12)-C(11)	119.1(3)
C(18)-C(13)-C(14)	117.6(3)
C(18)-C(13)-C(12)	123.8(3)
C(14)-C(13)-C(12)	118.6(3)
C(15)-C(14)-C(13)	121.1(3)
C(15)-C(14)-H(14)	119.4

C(13)-C(14)-H(14)	119.4
C(14)-C(15)-C(16)	121.5(3)
C(14)-C(15)-H(15)	119.3
C(16)-C(15)-H(15)	119.3
C(17)-C(16)-C(15)	116.9(3)
C(17)-C(16)-C(19)	121.6(3)
C(15)-C(16)-C(19)	121.5(3)
C(18)-C(17)-C(16)	122.3(3)
C(18)-C(17)-H(17)	118.8
C(16)-C(17)-H(17)	118.8
C(17)-C(18)-C(13)	120.5(3)
C(17)-C(18)-H(18)	119.7
C(13)-C(18)-H(18)	119.7
C(16)-C(19)-H(19A)	109.4
C(16)-C(19)-H(19B)	109.6
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for N191217A.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	54(1)	48(1)	39(1)	2(1)	16(1)	4(1)
N(1)	38(1)	33(1)	34(2)	0(1)	7(1)	1(1)
N(2)	44(2)	39(2)	50(2)	-4(1)	18(1)	-3(1)
O(1)	70(2)	66(2)	48(2)	22(1)	19(1)	30(1)
C(1)	37(2)	33(2)	34(2)	4(1)	9(1)	5(1)
C(2)	44(2)	38(2)	46(2)	6(2)	14(2)	-6(2)
C(3)	43(2)	27(2)	49(2)	-4(2)	6(2)	-2(1)
C(4)	38(2)	26(2)	36(2)	0(1)	3(1)	5(1)
C(5)	31(2)	29(2)	35(2)	6(1)	3(1)	2(1)
C(6)	32(2)	28(2)	38(2)	0(1)	4(1)	1(1)
C(7)	40(2)	45(2)	45(2)	-9(2)	11(2)	-5(2)
C(8)	51(2)	44(2)	65(3)	-7(2)	10(2)	-15(2)
C(9)	43(2)	49(2)	69(3)	9(2)	15(2)	-7(2)
C(10)	55(2)	52(2)	57(2)	3(2)	23(2)	0(2)
C(11)	41(2)	34(2)	38(2)	-9(1)	4(2)	0(1)
C(12)	43(2)	23(2)	41(2)	0(1)	10(2)	3(1)
C(13)	40(2)	26(2)	38(2)	-2(1)	4(1)	-1(1)
C(14)	44(2)	40(2)	45(2)	4(2)	6(2)	3(2)
C(15)	41(2)	46(2)	62(3)	-10(2)	10(2)	5(2)
C(16)	42(2)	52(2)	48(2)	-17(2)	9(2)	-5(2)
C(17)	59(2)	62(3)	39(2)	3(2)	9(2)	5(2)
C(18)	49(2)	54(2)	41(2)	3(2)	6(2)	13(2)
C(19)	60(2)	102(4)	61(3)	-14(2)	22(2)	2(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for N191217A.

	x	y	z	U(eq)
H(2)	6892	7779	3213	51
H(3)	6118	8634	4407	48
H(7)	3258	3460	3447	52
H(8)	1642	2086	3907	63
H(9)	628	2948	5011	64
H(10)	1289	5061	5643	64
H(11A)	4920	8451	5489	45
H(11B)	4283	6965	5656	45
H(14)	1099	10076	5299	51
H(15)	-103	10388	6379	59
H(17)	2104	7700	7772	64
H(18)	3320	7380	6701	57
H(19A)	-316	10172	7875	110
H(19B)	533	9073	8415	110
H(19C)	-619	8509	7830	110

Table 6. Torsion angles [deg] for N191217A.

C(5)-N(1)-C(1)-C(2)	0.6(4)
C(5)-N(1)-C(1)-Br(1)	179.5(2)
N(1)-C(1)-C(2)-C(3)	0.6(5)
Br(1)-C(1)-C(2)-C(3)	-178.2(2)
C(1)-C(2)-C(3)-C(4)	-0.9(5)
C(2)-C(3)-C(4)-C(5)	0.2(4)
C(2)-C(3)-C(4)-C(11)	179.1(3)
C(1)-N(1)-C(5)-C(4)	-1.5(4)
C(1)-N(1)-C(5)-C(6)	180.0(2)
C(3)-C(4)-C(5)-N(1)	1.1(4)
C(11)-C(4)-C(5)-N(1)	-177.8(3)
C(3)-C(4)-C(5)-C(6)	179.4(3)
C(11)-C(4)-C(5)-C(6)	0.5(4)
C(10)-N(2)-C(6)-C(7)	1.2(5)
C(10)-N(2)-C(6)-C(5)	-178.8(3)
N(1)-C(5)-C(6)-N(2)	-175.5(3)
C(4)-C(5)-C(6)-N(2)	6.0(4)
N(1)-C(5)-C(6)-C(7)	4.6(4)
C(4)-C(5)-C(6)-C(7)	-173.9(3)
N(2)-C(6)-C(7)-C(8)	-1.5(5)
C(5)-C(6)-C(7)-C(8)	178.4(3)
C(6)-C(7)-C(8)-C(9)	1.4(5)
C(7)-C(8)-C(9)-C(10)	-1.1(5)
C(6)-N(2)-C(10)-C(9)	-0.8(5)
C(8)-C(9)-C(10)-N(2)	0.8(6)
C(5)-C(4)-C(11)-C(12)	-70.9(4)
C(3)-C(4)-C(11)-C(12)	110.3(3)
C(4)-C(11)-C(12)-O(1)	-24.4(4)
C(4)-C(11)-C(12)-C(13)	160.1(3)
O(1)-C(12)-C(13)-C(18)	170.7(3)
C(11)-C(12)-C(13)-C(18)	-13.8(4)
O(1)-C(12)-C(13)-C(14)	-9.1(4)
C(11)-C(12)-C(13)-C(14)	166.4(3)
C(18)-C(13)-C(14)-C(15)	-2.0(5)
C(12)-C(13)-C(14)-C(15)	177.8(3)
C(13)-C(14)-C(15)-C(16)	0.2(5)
C(14)-C(15)-C(16)-C(17)	1.6(5)
C(14)-C(15)-C(16)-C(19)	-177.8(3)
C(15)-C(16)-C(17)-C(18)	-1.5(5)
C(19)-C(16)-C(17)-C(18)	177.9(3)
C(16)-C(17)-C(18)-C(13)	-0.4(6)
C(14)-C(13)-C(18)-C(17)	2.1(5)

C(12)-C(13)-C(18)-C(17)	-177.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for N191217A [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-Ray crystallographic data of **3ea**:

Table 8 Crystal data and structure refinement for A200710A.

Identification code	A200710A
Empirical formula	$C_{19}H_{16}N_2O_2$
Formula weight	304.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.8361(10)
b/Å	8.2497(8)
c/Å	21.719(2)
α/°	90
β/°	96.488(11)
γ/°	90
Volume/Å^3	1573.1(3)
Z	4
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.085
F(000)	640.0
Crystal size/mm^3	0.2 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.64 to 50.018
Index ranges	$-8 \le h \le 10$, $-9 \le k \le 9$, $-25 \le l \le 25$
Reflections collected	7217
Independent reflections	2776 [R_{int} = 0.0245, R_{sigma} = 0.0281]
Data/restraints/parameters	2776/0/209
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0485, wR_2 = 0.1378
Final R indexes [all data]	R_1 = 0.0714, wR_2 = 0.1575
Largest diff. peak/hole / e Å^{-3}	0.14/-0.17

Table 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for A200710A. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O1	9776.0(18)	3251.5(18)	3854.5(8)	77.0(5)
O2	5445.4(18)	8329.5(16)	4676.5(7)	69.7(4)
N1	6305(2)	2447(2)	3309.3(10)	84.7(6)
N2	5485.4(18)	5884.0(18)	4167.0(7)	53.3(4)
C1	9489(2)	415(2)	3770.9(9)	55.5(5)
C2	10431(3)	321(3)	3309.7(12)	79.9(7)
C3	10829(3)	-1159(3)	3077.1(14)	96.0(9)
C4	10290(3)	-2566(3)	3311.0(12)	77.5(7)
C5	9346(3)	-2487(3)	3761.3(12)	72.2(6)
C6	8939(3)	-1015(2)	3988.4(10)	65.2(6)
C7	9115(2)	2056(2)	4013.1(9)	57.3(5)
C8	7995(2)	2170(2)	4484.4(10)	64.5(6)
C9	7299(2)	3823(2)	4534.2(9)	55.3(5)
C10	6112(2)	4394(2)	4116.3(8)	50.4(5)
C11	6031(2)	6823(2)	4627.7(9)	55.7(5)
C12	7203(2)	6370(3)	5070.9(9)	61.2(6)
C13	7833(2)	4868(3)	5018.3(9)	61.5(6)
C14	5413(2)	3467(2)	3572.8(9)	54.6(5)
C15	5719(4)	1700(4)	2791.6(16)	112.5(11)
C16	4247(4)	1892(4)	2532.2(14)	102.3(10)
C17	3322(3)	2911(3)	2809.1(11)	77.8(7)
C18	3909(3)	3716(2)	3342.3(10)	61.5(6)
C19	4282(3)	8815(3)	4201.2(12)	80.1(7)

Table 10 Anisotropic Displacement Parameters ($Å^2×10^3$) for A200710A. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	75.7(10)	62.3(9)	96.2(12)	1.1(8)	23.4(9)	-17.5(8)
O2	83(1)	58.1(8)	67.6(10)	-15.9(7)	6.6(8)	1.5(7)
N1	86.7(13)	76.0(13)	90.5(15)	-37.6(11)	6.1(12)	0.3(11)
N2	58.6(10)	51.5(9)	50.1(9)	-4.1(7)	8.1(8)	-5.5(8)
C1	47.1(11)	60.3(12)	58.0(12)	7.6(9)	1.6(9)	-1.1(9)
C2	79.0(15)	70.9(15)	94.9(18)	10.5(13)	31.5(14)	-0.5(12)
C3	97(2)	96(2)	103(2)	0.9(16)	42.0(17)	15.4(16)
C4	75.4(15)	70.2(15)	84.9(17)	-3.7(13)	0.0(14)	18.4(13)
C5	77.7(15)	57.2(13)	80.0(16)	9.1(11)	2.0(13)	4.2(11)
C6	69.9(13)	58.2(12)	68.9(14)	7.3(10)	13.3(11)	-1.3(10)
C7	53.8(11)	57.2(11)	59.8(13)	9.5(10)	1.8(10)	-2.9(10)
C8	70.2(13)	60.8(12)	63.8(14)	7.6(10)	13.4(11)	0(1)
C9	59.8(12)	55.1(11)	52.4(12)	3.6(9)	11.9(10)	-5.2(9)
C10	55.4(11)	50.4(11)	46.8(11)	-0.8(8)	12.0(9)	-8.9(9)
C11	63.0(12)	55.1(11)	50.3(12)	-6.6(9)	12.6(10)	-8.4(10)
C12	69.1(13)	67.1(13)	47.7(12)	-8.9(10)	7.9(10)	-12.2(11)
C13	63.6(13)	74.5(14)	46.2(11)	3.3(10)	5.3(10)	-6.1(11)
C14	66.0(13)	47.5(10)	51.4(12)	-2.3(9)	11.5(10)	-9.6(9)
C15	121(2)	103(2)	111(2)	-61.1(19)	1(2)	0.1(18)
C16	133(3)	87.8(18)	82.4(19)	-37.3(15)	-4.3(19)	-28.6(18)
C17	87.3(16)	77.1(15)	65.2(15)	4.5(12)	-8.3(13)	-29.0(13)
C18	68.9(14)	61.9(12)	53.2(12)	2.7(10)	4.7(11)	-11.2(10)
C19	93.8(18)	66.7(14)	77.7(17)	-10.5(12)	0.7(14)	12.7(12)

Table 11 Bond Lengths for A200710A.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.216(2)	C5	C6	1.374(3)
O2	C11	1.355(2)	C7	C8	1.505(3)
O2	C19	1.429(3)	C8	C9	1.505(3)
N1	C14	1.326(3)	C9	C10	1.390(3)
N1	C15	1.335(3)	C9	C13	1.400(3)
N2	C10	1.357(2)	C10	C14	1.481(3)
N2	C11	1.313(2)	C11	C12	1.384(3)
C1	C2	1.375(3)	C12	C13	1.368(3)
C1	C6	1.379(3)	C14	C18	1.382(3)
C1	C7	1.502(3)	C15	C16	1.367(4)
C2	C3	1.382(4)	C16	C17	1.359(4)
C3	C4	1.374(4)	C17	C18	1.384(3)
C4	C5	1.357(3)			

Table 12 Bond Angles for A200710A.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	O2	C19	116.76(16)	C13	C9	C8	120.45(19)
C14	N1	C15	117.6(2)	N2	C10	C9	122.60(17)
C11	N2	C10	118.57(18)	N2	C10	C14	113.28(17)
C2	C1	C6	117.8(2)	C9	C10	C14	124.12(17)
C2	C1	C7	118.74(18)	O2	C11	C12	117.12(17)
C6	C1	C7	123.41(18)	N2	C11	O2	119.36(19)
C1	C2	C3	121.1(2)	N2	C11	C12	123.51(18)
C4	C3	C2	119.9(2)	C13	C12	C11	117.78(18)
C5	C4	C3	119.5(2)	C12	C13	C9	121.0(2)
C4	C5	C6	120.5(2)	N1	C14	C10	117.20(18)
C5	C6	C1	121.1(2)	N1	C14	C18	122.16(19)
O1	C7	C1	120.03(18)	C18	C14	C10	120.59(18)
O1	C7	C8	121.04(19)	N1	C15	C16	123.6(3)
C1	C7	C8	118.80(17)	C17	C16	C15	118.8(2)
C9	C8	C7	114.26(16)	C16	C17	C18	118.7(2)
C10	C9	C8	123.01(18)	C14	C18	C17	119.1(2)
C10	C9	C13	116.53(18)				

Table 13 Torsion Angles for A200710A.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C7	C8	C9	24.0(3)	C8	C9	C10	N2	179.61(17)
O2	C11	C12	C13	-178.34(17)	C8	C9	C10	C14	-1.0(3)
N1	C14	C18	C17	-1.8(3)	C8	C9	C13	C12	-179.60(18)
N1	C15	C16	C17	0.7(5)	C9	C10	C14	N1	-31.0(3)
N2	C10	C14	N1	148.47(19)	C9	C10	C14	C18	151.44(19)
N2	C10	C14	C18	-29.1(2)	C10	N2	C11	O2	178.34(16)
N2	C11	C12	C13	0.8(3)	C10	N2	C11	C12	-0.7(3)
C1	C2	C3	C4	-0.5(4)	C10	C9	C13	C12	0.1(3)
C1	C7	C8	C9	-160.15(18)	C10	C14	C18	C17	175.65(17)
C2	C1	C6	C5	1.4(3)	C11	N2	C10	C9	0.4(3)
C2	C1	C7	O1	-8.5(3)	C11	N2	C10	C14	-179.07(16)
C2	C1	C7	C8	175.6(2)	C11	C12	C13	C9	-0.4(3)
C2	C3	C4	C5	1.2(4)	C13	C9	C10	N2	0.0(3)
C3	C4	C5	C6	-0.6(4)	C13	C9	C10	C14	179.34(17)
C4	C5	C6	C1	-0.7(4)	C14	N1	C15	C16	-2.0(5)
C6	C1	C2	C3	-0.8(4)	C15	N1	C14	C10	-175.0(2)
C6	C1	C7	O1	171.3(2)	C15	N1	C14	C18	2.6(3)
C6	C1	C7	C8	-4.6(3)	C15	C16	C17	C18	0.2(4)
C7	C1	C2	C3	179.0(2)	C16	C17	C18	C14	0.4(3)
C7	C1	C6	C5	-178.39(19)	C19	O2	C11	N2	-1.9(3)
C7	C8	C9	C10	79.4(2)	C19	O2	C11	C12	177.26(19)
C7	C8	C9	C13	-101.0(2)					

Table 14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for A200710A.

Atom	*x*	*y*	*z*	U(eq)
H2	10806	1269	3152	96
H3	11461	-1202	2763	115
H4	10571	-3566	3162	93
H5	8971	-3438	3918	87
H6	8282	-982	4294	78
H8A	7185	1391	4378	77
H8B	8508	1868	4887	77
H12	7552	7064	5394	73
H13	8627	4537	5309	74
H15	6347	1009	2597	135
H16	3886	1336	2173	123
H17	2315	3063	2644	93

H18	3299	4415	3543	74
H19A	4674	8780	3807	120
H19B	3961	9899	4281	120
H19C	3429	8091	4196	120

X-Ray crystallographic data of **4aa**:

Table 15 Crystal data and structure refinement for A200108A.

Identification code	A200108A
Empirical formula	$C_{18}H_{11}BrN_2O$
Formula weight	351.20
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7732(5)
b/Å	7.7539(3)
c/Å	15.9751(7)
α/°	90
β/°	104.728(4)
γ/°	90
Volume/Å^3	1410.43(10)
Z	4
ρ_{calc}g/cm^3	1.654
μ/mm^{-1}	3.992
F(000)	704.0
Crystal size/mm^3	0.18 × 0.17 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.764 to 134.09
Index ranges	$-13 \leq h \leq 14$, $-6 \leq k \leq 9$, $-19 \leq l \leq 18$
Reflections collected	4725
Independent reflections	2512 [R_{int} = 0.0850, R_{sigma} = 0.0876]
Data/restraints/parameters	2512/0/199
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0845, wR_2 = 0.2077
Final R indexes [all data]	R_1 = 0.0943, wR_2 = 0.2305
Largest diff. peak/hole / e Å^{-3}	1.57/-1.71

Table 16 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for A200108A. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Br1	2333.8(4)	8755.3(7)	4567.1(4)	25.8(3)
O1	9377(3)	6370(5)	5591(3)	25.3(9)
N1	7156(4)	5626(6)	4390(3)	18.9(9)
N2	4273(4)	7214(5)	4237(3)	20.5(9)
C1	5998(5)	5851(7)	3908(3)	20.3(11)
C2	5643(5)	5199(7)	3064(4)	24.8(11)
C3	6431(5)	4343(7)	2716(3)	27.0(12)
C4	7593(5)	4112(7)	3221(4)	24.2(11)
C5	7942(4)	4764(7)	4048(4)	23.8(11)
C6	7308(5)	6284(6)	5233(4)	19.0(11)
C7	6210(4)	6945(7)	5269(4)	21.1(11)
C8	5411(4)	6698(7)	4462(3)	19.4(10)
C9	3933(4)	8006(6)	4853(3)	20.2(10)
C10	4645(5)	8400(7)	5687(3)	20.3(10)
C11	5795(4)	7860(6)	5898(3)	20.2(10)
C12	8467(5)	6383(6)	5826(4)	19.0(12)
C13	8531(5)	6499(7)	6769(4)	20.1(11)
C14	7830(4)	5458(6)	7148(3)	20.9(11)
C15	8005(4)	5463(7)	8044(4)	23.1(11)
C16	8850(5)	6487(8)	8567(4)	24.8(12)
C17	9537(5)	7558(7)	8190(4)	26.4(11)
C18	9389(4)	7539(7)	7296(4)	24.1(11)

Table 17 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for A200108A. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	10.1(5)	28.4(5)	35.0(5)	3.5(2)	-1.3(3)	1.54(17)
O1	12.0(19)	35(2)	27(2)	0.2(16)	0.5(16)	1.6(14)
N1	13.1(19)	19(2)	21.7(19)	1.9(18)	-1.2(16)	-2.2(17)
N2	13.3(19)	18(2)	26(2)	1.3(17)	-3.3(17)	-2.8(16)
C1	16(3)	19(2)	22(3)	6(2)	-2(2)	-4(2)
C2	20(2)	26(3)	24(2)	1(2)	-2(2)	-3(2)
C3	35(3)	24(3)	20(2)	-3(2)	4(2)	-3(2)
C4	28(3)	21(2)	27(3)	1(2)	13(2)	0(2)
C5	16(2)	21(2)	33(3)	-1(2)	4(2)	-1(2)
C6	16(3)	16(3)	22(3)	-0.2(18)	0(2)	0.1(18)
C7	14(2)	21(2)	25(2)	4(2)	-1(2)	-5(2)
C8	12(2)	20(2)	22(2)	2(2)	-2(2)	-4(2)
C9	13(2)	21(2)	23(2)	8(2)	-2.2(19)	-0.4(19)
C10	16(2)	21(2)	24(3)	0(2)	4(2)	-2(2)
C11	11(2)	20(2)	25(2)	0(2)	-5.2(19)	-1.9(18)
C12	9(3)	15(2)	30(3)	3.6(18)	1(2)	0.0(16)
C13	11(2)	23(2)	24(3)	3(2)	-1(2)	3.5(19)
C14	13(2)	21(2)	25(3)	-1(2)	-3(2)	0.2(19)
C15	17(2)	22(3)	29(3)	3(2)	4(2)	3.0(19)
C16	19(3)	29(3)	21(3)	0(2)	-4(2)	7(2)
C17	15(2)	25(2)	31(3)	-5(2)	-8(2)	1(2)
C18	13(2)	24(2)	32(3)	-1(2)	-1(2)	-2(2)

Table 18 Bond Lengths for A200108A.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.912(5)	C6	C12	1.452(7)
O1	C12	1.223(7)	C7	C8	1.402(8)
N1	C1	1.396(7)	C7	C11	1.414(8)
N1	C5	1.364(7)	C9	C10	1.415(8)
N1	C6	1.408(7)	C10	C11	1.374(7)
N2	C8	1.356(7)	C12	C13	1.491(8)
N2	C9	1.306(7)	C13	C14	1.398(8)
C1	C2	1.401(8)	C13	C18	1.395(8)
C1	C8	1.415(8)	C14	C15	1.393(7)
C2	C3	1.369(9)	C15	C16	1.377(8)
C3	C4	1.413(8)	C16	C17	1.398(9)
C4	C5	1.375(8)	C17	C18	1.394(8)
C6	C7	1.405(8)			

Table 19 Bond Angles for A200108A.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C6	110.5(4)	N2	C8	C7	126.1(5)
C5	N1	C1	120.5(5)	C7	C8	C1	108.6(5)
C5	N1	C6	128.8(5)	N2	C9	Br1	115.8(4)
C9	N2	C8	114.2(4)	N2	C9	C10	126.1(5)
N1	C1	C2	119.7(5)	C10	C9	Br1	118.1(4)
N1	C1	C8	106.1(4)	C11	C10	C9	118.4(5)
C2	C1	C8	134.1(5)	C10	C11	C7	118.4(5)
C3	C2	C1	120.0(5)	O1	C12	C6	123.4(6)
C2	C3	C4	119.2(5)	O1	C12	C13	119.2(5)
C5	C4	C3	120.8(5)	C6	C12	C13	117.4(5)
N1	C5	C4	119.9(5)	C14	C13	C12	121.3(5)
N1	C6	C12	120.9(5)	C18	C13	C12	119.2(5)
C7	C6	N1	106.1(5)	C18	C13	C14	119.2(5)
C7	C6	C12	132.4(5)	C15	C14	C13	119.6(5)
C6	C7	C11	134.4(5)	C16	C15	C14	121.3(5)
C8	C7	C6	108.7(5)	C15	C16	C17	119.3(5)
C8	C7	C11	116.7(5)	C18	C17	C16	120.0(5)
N2	C8	C1	125.3(5)	C17	C18	C13	120.5(5)

Table 20 Torsion Angles for A200108A.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Br1	C9	C10	C11	179.8(4)	C6	C7	C8	N2	-177.8(5)
O1	C12	C13	C14	-135.8(5)	C6	C7	C8	C1	0.8(6)
O1	C12	C13	C18	37.6(7)	C6	C7	C11	C10	176.3(6)
N1	C1	C2	C3	0.0(8)	C6	C12	C13	C14	43.9(7)
N1	C1	C8	N2	177.6(5)	C6	C12	C13	C18	-142.7(5)
N1	C1	C8	C7	-1.0(6)	C7	C6	C12	O1	-149.7(6)
N1	C6	C7	C8	-0.3(6)	C7	C6	C12	C13	30.6(8)
N1	C6	C7	C11	-175.3(5)	C8	N2	C9	Br1	-179.9(3)
N1	C6	C12	O1	20.4(7)	C8	N2	C9	C10	2.4(7)
N1	C6	C12	C13	-159.3(4)	C8	C1	C2	C3	-176.4(6)
N2	C9	C10	C11	-2.6(8)	C8	C7	C11	C10	1.6(7)
C1	N1	C5	C4	0.0(8)	C9	N2	C8	C1	-178.5(5)
C1	N1	C6	C7	-0.3(5)	C9	N2	C8	C7	-0.2(7)
C1	N1	C6	C12	-172.8(4)	C9	C10	C11	C7	0.3(7)
C1	C2	C3	C4	0.8(8)	C11	C7	C8	N2	-1.8(8)
C2	C1	C8	N2	-5.7(10)	C11	C7	C8	C1	176.8(4)
C2	C1	C8	C7	175.8(6)	C12	C6	C7	C8	170.9(5)
C2	C3	C4	C5	-1.3(9)	C12	C6	C7	C11	-4.1(10)
C3	C4	C5	N1	0.8(8)	C12	C13	C14	C15	172.9(5)
C5	N1	C1	C2	-0.5(7)	C12	C13	C18	C17	-174.4(5)
C5	N1	C1	C8	176.8(5)	C13	C14	C15	C16	0.6(8)
C5	N1	C6	C7	-175.9(5)	C14	C13	C18	C17	-0.9(8)
C5	N1	C6	C12	11.6(8)	C14	C15	C16	C17	0.7(8)
C6	N1	C1	C2	-176.5(5)	C15	C16	C17	C18	-2.1(8)
C6	N1	C1	C8	0.8(6)	C16	C17	C18	C13	2.2(8)
C6	N1	C5	C4	175.3(5)	C18	C13	C14	C15	-0.6(7)

Table 21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for A200108A.

Atom	*x*	*y*	*z*	U(eq)
H2	4872	5346	2741	30
H3	6204	3919	2153	32
H4	8129	3512	2992	29
H5	8712	4617	4372	29
H10	4343	9010	6083	24
H11	6288	8090	6441	24
H14	7250	4766	6805	25
H15	7542	4759	8295	28
H16	8963	6468	9165	30
H17	10093	8283	8535	32
H18	9866	8223	7049	29