Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Transition-Metal-Free C–H Amidation and Chlorination: Synthesis of *N/N'*-Mono-Substituted Imidazopyridin-2-ones from *N*-Pyridyl-*N*-hydroxylamine Intermediates

Katarzyna N. Lee,[a] Dominique N. Spiegowski,[a] Johnny W. Lee,[a] Sanghyun Lim,[a] Fuhua Zhao,[a] and Ming-Yu Ngai*[a,b]

ming-yu.ngai@stonybrook.edu

[a]Department of Chemistry, State University of New York,
Stony Brook, New York 11794-3400

[b]Institute of Chemical Biology and Drug Discovery, State University of New York,
Stony Brook, New York 11794-3400

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General Information

All air- and moisture-insensitive reactions were carried out under an ambient atmosphere, magnetically stirred, and monitored by thin layer chromatography (TLC) using Agela Technologies TLC plates pre-coated with 250 μm thickness silica gel 60 F254 plates and visualized by fluorescence quenching under UV light. Flash chromatography was performed on SiliaFlash® Silica Gel 40-63μm 60Å particle size using a forced flow of eluent at 0.3–0.5 bar pressure.[1] Preparative TLC was performed on Uniplate® UV254 (20 x 20 cm) with 1000 μm thickness and visualized fluorescence quenching under UV light.

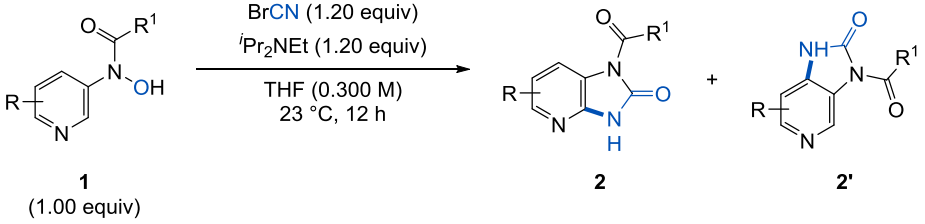
All air and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. All reaction vials were capped using green caps with F-217 PTFE liners. THF was distilled from deep purple sodium benzophenone ketyl.

All deuterated solvents were purchased from Cambridge Isotope Laboratories. NMR spectra were recorded on either a Bruker Ascend 700 spectrometer operating at 700 MHz for ^{1}H acquisitions and 175 MHz for ^{13}C acquisitions, a Bruker 500 Advance spectrometer operating at 500 MHz, 125 MHz, and 470 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively, a Bruker 400 Nanobay spectrometer operating at 400 MHz, 100 MHz, and 376 MHz for ^{1}H, ^{13}C, and ^{19}F acquisitions, respectively. Chemical shifts were referenced to the residual proton solvent peaks (^{1}H: $CDCl_3$, δ 7.26; $(CD_3)_2SO$, δ 2.50;), solvent ^{13}C signals ($CDCl_3$, δ 77.16; $(CD_3)_2SO$, δ 39.52),[2] dissolved or external neat $PhCF_3$ (^{19}F, δ –63.3 relative to $CFCl_3$).[3] Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet; coupling constants in Hz; integration.

High-resolution mass spectra were performed at Mass Spectrometry Services at the Univ. of Illinois at Urbana-Champaign and were obtained using Waters Q-TOF Ultima ESI mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 ºC at appropriate pressure. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds.

Experimental Data

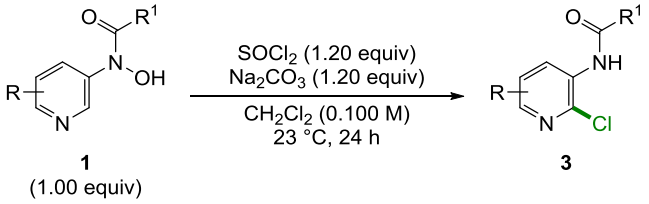
General Procedure A:



In a glovebox, to an oven-dried 20 mL screw cap vial were added *N*-protected *N*-pyridyl-*N*-hydroxylamine (**1**, 0.300 mmol, 1.00 equiv), *N*,*N*-diisopropylethylamine ($^{i}Pr_2NEt$) (62.7 μL, 46.5 mg, 0.360 mmol, 1.20 equiv) and THF (1.00 mL, 0.300 M, with respect to hydroxylamine substrate). To this suspension were added cyanogen bromide (38.1 mg, 0.360 mmol, 1.20 equiv) and a magnetic stir bar. The reaction vial was

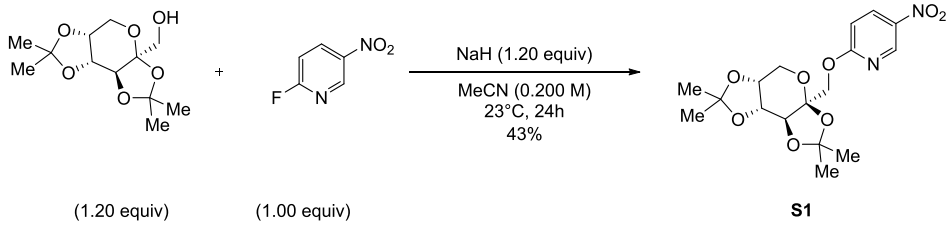
then capped and taken out of the glovebox. After the reaction mixture was stirred at 23 °C for 12 h, it was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel with gradient eluents to afford the desired product **2** or **2'**.

General Procedure B:



In a glovebox, to a 20 mL oven-dried screw cap vial charged with a magnetic stir bar were added *N*-protected *N*-pyridyl-*N*-hydroxylamine (**1**, 0.300 mmol, 1.00 equiv), sodium carbonate (38.2 mg, 0.400 mmol, 1.20 equiv), and CH_2Cl_2 (3.00 mL, 0.100 M). Thionyl chloride (26.0 μL 0.400 mmol, 1.20 equiv) was then added to the suspension, the vial was capped and removed from the glovebox. After the reaction mixture was stirred at 23 °C for 2-24 h, it was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with EtOAc:Hexanes to afford the desired product of chlorination **3**.

5-Nitro-2-((3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methoxy)pyridine (S1)

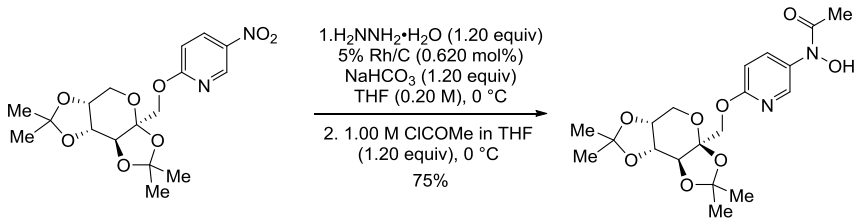


Under nitrogen atmosphere, NaH (0.768 g, 19.2 mmol, 1.20 equiv, 60% dispersion in mineral oil), (3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methanol (4.16 g, 16.0 mmol, 1.00 equiv) and MeCN (0.200 M, 80.0 mL) were added to a 200 mL round bottom flask. To this suspension, 2-fluoro-5-nitropyridine (2.27 mL, 16.0 mmol. 1.00 equiv) was added dropwise and the resulting mixture was stirred vigorously with a stir bar at 60 °C for 24 h. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with EtOAc:Hexanes [1:4 (v/v)], to afford the title compound as a white solid (2.65 g, 6.88 mmol, 43% yield).

R_f = 0.35 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 9.07 (d, *J* = 2.7 Hz, 1H), 8.50 (dd, *J* = 2.8, 9.1 Hz, 1H), 7.06 (d, *J* = 9.1 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.61 (dd, *J* = 2.3, 7.9 Hz, 1H), 4.42 (d, *J* = 2.4 Hz, 1H), 4.27 (d, *J* = 11.3 Hz, 1H), 4.26 (d, *J* = 7.4 Hz, 1H), 3.78 (d, *J* = 12.0 Hz, 1H),

3.63 (d, *J* = 13.0 Hz, 1H), 1.45 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 166.44, 144.97, 140.24, 135.43, 111.97, 108.75, 108.62, 101.61, 70.50, 70.40, 69.73, 67.94, 60.98, 26.68, 26.19, 25.49 , 24.40. **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{22}N_2O_8$ [$(M + H)^+$], 383.1449, found, 383.1447.

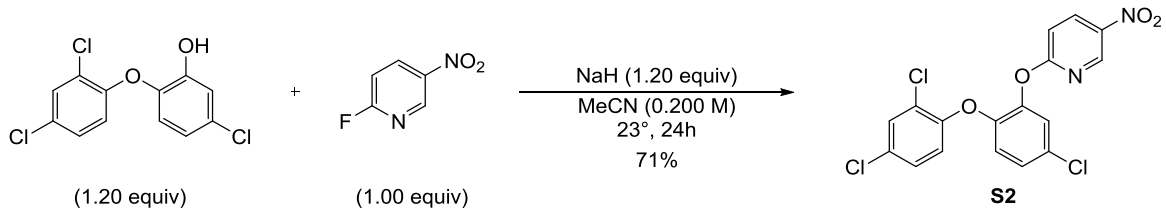
_N_-Hydroxy-_N_-(6-(((3_aS_,5_aR_,8_aR_,8_bS_)-2,2,7,7-tetramethyltetrahydro-3_aH_-bis([1,3]dioxolo)[4,5-_b_:4',5'-_d_]pyran-3_a_-yl)methoxy)pyridine-3-yl)acetamide (1p)



Under nitrogen atmosphere, a suspension of 5-Nitro-2-(((3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methoxy)pyridine (0.588 g, 1.50 mmol, 1.00 equiv), 5% Rh/C (30.9 mg, 0.0200 mmol, 0.620 mol%), and $NaHCO_3$ (0.151 g, 1.80 mmol, 1.20 equiv) in THF (0.200 M, 7.50 mL) was cooled to 0 °C in an ice bath. Hydrazine monohydrate (87.3 μL, 1.80 mmol, 1.20 equiv) was then added dropwise and the reaction mixture was stirred vigorously with a stir bar at 0 °C for 1 h. While the reaction flask was still in the ice bath, a solution of acetyl chloride (0.128 mL, 1.80 mol, 1.20 equiv) in THF (1.00 M, 1.80 mL) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h and then warmed up to 23 °C. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel eluting with EtOAc:Hexanes [1:1 (v/v)] to afford the title compound as a white solid (0.460 g, 9.41 mmol, 75% yield).

R_f = 0.35 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 10.74 (s, 1H), 8.33 (s, 1H), 7.91 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 1H), 4.61 (dd, *J* = 1.9, 7.9 Hz, 1H), 4.50 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 1.8 Hz, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 4.13 (d, *J* = 11.2 Hz, 1H), 3.78 (d, *J* = 12.8 Hz, 1H), 3.63 (d, *J* = 13.0 Hz, 1H), 2.19 (s, 3H) ,1.46 (s, 3H), 1.37 (d, *J* = 5.1 Hz, 6H), 1.27 (s, 3H). **^{13}C NMR** (176 MHz, $(CD_3)_2SO$, 25 ºC) δ 139.50, 133.61, 133.13, 110.63, 108.57 (d, *J* = 6.1 Hz, 1C), 102.02, 70.59, 70.34, 69.81, 66.79, 60.87, 60.22, 26.75, 26.21, 25.59, 24.44, 22.25, 21.23, 14.55. **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{26}N_2O_8$ [$(M + H)^+$], 411.1762, found, 411.1761.

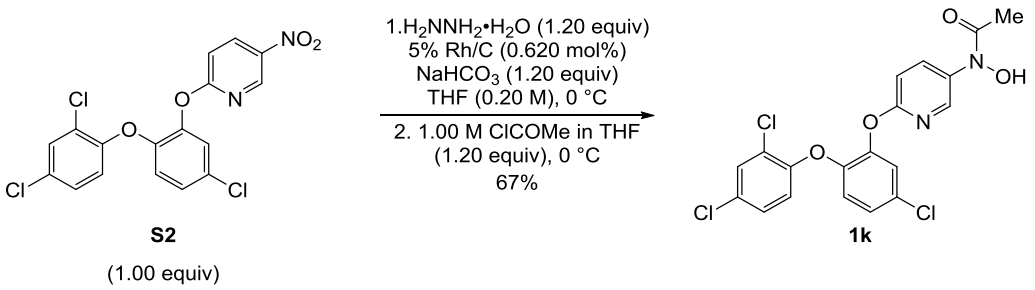
2-(5-Chloro-2-(2,4-dichlorophenoxy)phenoxy)-5-nitropyridine (S2)



Under nitrogen atmosphere, NaH (0.768 g, 19.2 mmol, 1.20 equiv, 60% dispersion in mineral oil), 5-chloro-2-(2,4-dichlorophenoxy)phenol (4.63 g, 16.0 mmol, 1.00 equiv) and MeCN (0.200 M, 80.0 mL) were added to a 200 mL round bottom flask. To this suspension, 2-fluoro-5-nitropyridine (2.27 mL, 16.0 mmol. 1.00 equiv) was added dropwise and the resulting mixture was stirred vigorously with a stir bar at 60 °C for 24 h. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with EtOAc:Hexanes [1:4 (v/v)], to afford the title compound as a white solid (4.65 g, 11.3 mmol, 71% yield).

R_f = 0.45 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 9.01 (d, *J* = 2.6 Hz, 1H), 8.60 (dd, *J* = 2.6, 9.1 Hz, 1H), 7.65 (dd, *J* = 2.1, 7.4 Hz, 2H), 7.41 (dd, *J*= 2.2, 8.8 Hz, 1H), 7.36 (dd, *J* = 2.2, 8.8 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 165.58, 150.78, 146.95, 144.88, 143.90, 141.41, 136.45, 130.44, 129.22, 129.06, 128.95, 127.73, 125.05, 124.93, 121.76, 121.09, 111.73. **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_9Cl_3N_2O_4$ $[(M + H)^+]$, 410.9701 found, 410.9706.

***N*-(6-(5-Chloro-2-(2,4-dichlorophenoxy)phenoxy)pyridine-3-yl)-*N*-hydroxyacetamide (1k)**

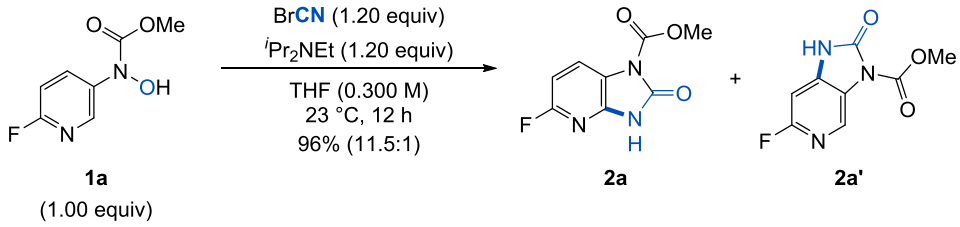


Under nitrogen atmosphere, a suspension of 2-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)-5-nitropyridine (288 mg, 0.700 mmol, 1.00 equiv), 5% Rh/C (4.00 mg, 0.0400 mmol, 0.620 mol%), and $NaHCO_3$ (69.7 mg, 0.840 mmol, 1.20 equiv) in THF (0.200 M, 3.50 mL) was cooled to 0 °C in an ice bath. Hydrazine monohydrate (42.1 μL, 0.840 mmol, 1.20 equiv) was then added dropwise and the reaction mixture was stirred vigorously with a stir bar at 0 °C for 1 h. While the reaction flask was still in the ice bath, a solution of acetyl chloride (59.9 μL, 0.840 mol, 1.20 equiv) in THF (1.00 M, 3.50 mL) was added dropwise and the

resulting mixture was stirred at 0 °C for 2 h and then warmed up to 23 °C. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel eluting with EtOAc:Hexanes [1:5 to 1:1 (v/v)] to afford the title compound as a white solid (0.207 g, 0.469 mmol, 67% yield).

R_f = 0.45 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 10.77 (s, 1H), 8.30 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.65 (s, 1H), 7.51 (s, 1H), 7.34 (m, *J* = 3.7 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 6.96 (dd, *J* = 8.9, 17.6 Hz, 2H), 2.18 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 170.82, 151.27, 146.93, 145.21, 135.13, 130.33, 129.10, 129.03, 128.43, 126.72, 124.84, 124.71, 122.10, 120.46, 110.63, 60.23, 22.35, 21.24, 14.55. **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{13}Cl_3N_2O_4$ [$(M + H)^+$], 439.0014, found, 439.0014.

Methyl 5-fluoro-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridine-1-carboxylate (2a) and methyl 6-fluoro-2-oxo-1*H*-imidazo[4,5-*c*]pyridine-3(2*H*)-carboxylate (2a')



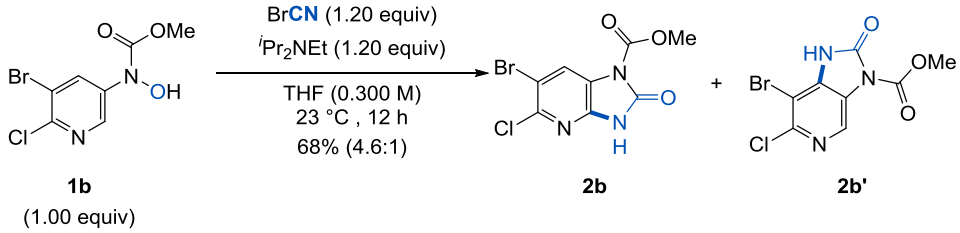
The reaction was performed according to the general procedure A using methyl (6-fluoropyridin-3-yl)(hydroxyl)carbamate (93.1 mg, 0.500 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [4:6 to 7:3 (v/v)] to afford the title compound **2a** as an off-white solid and a mixture of **2a** and **2a'** as a white solid (**2a**:**2a'**=11.5:1, 101.4 mg, 0.480 mmol, 96% yield).

2a: R_f = 0.34 EtOAc:Hexanes [7:3 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.20 (s, 1H), 8.02 (dd, *J* = 7.1, 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 160.08, 158.75, 149.97 (d, *J* = 35.4 Hz), 141.57 (d, *J* = 19.8 Hz), 125.33 (d, *J* = 7.8 Hz), 118.90 (d, *J* = 3.8 Hz), 100.52 (d, *J* = 37.8 Hz), 54.03. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$, 25 ºC) δ -80.04 (d, *J* = 6.5 Hz, 1F). **HRMS** (ESI-TOF) *m/z* calcd for $C_8H_7FN_3O_3$ [$(M + H)^+$], 212.0466, found, 212.0463.

A mixture of 2a and 2a': R_f = 0.34, 0.09 EtOAc:Hexanes [7:3 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.17 (s, 1.21H, **2a** and **2a'**), 8.30 (s, 0.15H, **2a'**), 8.01 (dd, *J* = 7.1, 8.4 Hz, 1H, **2a**), 6.82 (d, *J* = 8.4 Hz, 0.91H, **2a**), 6.80 (d, *J* = 1.8 Hz, 0.15H, **2a'**), 3.94 (s, 0.47H, **2a'**), 3.93 (s, 2.7H, **2a**). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 160.09, 159.72, 158.76, 158.43, 154.99 (d, *J* = 138.6 Hz), 149.98 (d, *J* = 54.6 Hz), 141.60 (d, *J* = 19.5 Hz), 139.95 (d, *J* = 11.7 Hz), 129.80 (d, *J* = 19.5 Hz), 125.33 (d, *J* = 9.1 Hz), 123.40 (d, *J* = 2.6 Hz) 118.91 (d, *J* = 3.8 Hz), 100.52 (d, *J* = 37.5 Hz), 90.04 (d, *J* = 48.3 Hz), 54.03. **^{19}F**

NMR (376 MHz, $(CD_3)_2SO$, 25 ºC) δ -72.98 (s, 0.17F), -80.02 (d, *J* = 6.8 Hz, 1F). Due to the poor solubility of the products in organic solvents, the minor isomer **2a'** was eluted together with the major isomer **2a**.

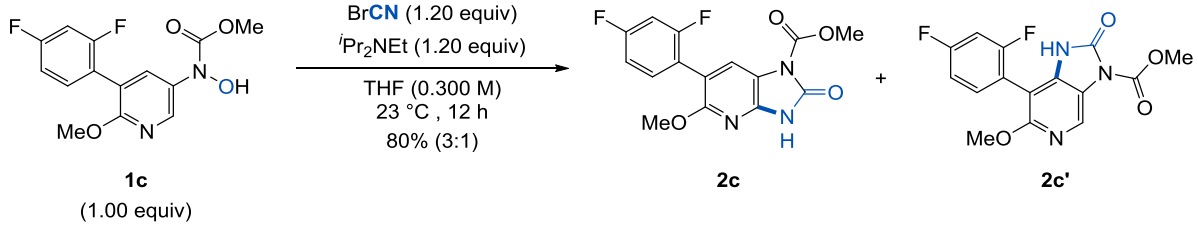
Methyl 6-bromo-5-chloro-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridine-1-carboxylate (2b) and methyl 7-bromo-6-chloro-2-oxo-1*H*-imidazo[4,5-*c*]pyridine-3(2*H*)-carboxylate (2b')



The reaction was performed according to the general procedure A using methyl (5-bromo-6-chloropyridin-3-yl)(hydroxy)carbamate (84.4 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [4:6 (v/v)] to afford the mixture of title compound **2b** and **2b'** as an off-white solid (**2b**:**2b'**=4.6:1, 62.6 mg, 0.204 mmol, 68% yield).

A mixture of 2b and 2b': R_f = 0.30 EtOAc:Hexanes [7:3 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.42 (s, 1.46H, **2b** and **2b'**), 8.48 (s, 0.22H, **2b'**), 8.08 (s, 1H, **2b**), 3.96 (s, 1.04H, **2b'**), 3.95 (s, 3H, **2b**). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 149.83, 149.77, 149.47, 143.25, 142.82, 141.89, 131.01, 125.43, 124.51, 121.61, 109.88, 98.55, 54.33, 54.29. Due to similar R_f, the major and minor isomers were eluted together. **HRMS** (ESI-TOF) *m/z* calcd for $C_8H_4BrClN_3O_3$ [(M - H)$^-$], 303.913, found, 303.9131.

Methyl-6-(2,4-difluorophenyl)-5-methoxy-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridine-1-carboxylate (2c) and methyl 7-(2,4-difluorophenyl)-6-methoxy-2-oxo-1*H*-imidazo[4,5-*c*]pyridine-3(2*H*)-carboxylate (2c')

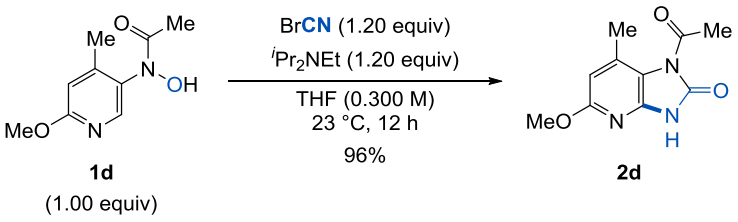


The reaction was performed according to the general procedure A using methyl (5-(2,4-difluorophenyl)-6-methoxypyridin-3-yl)(hydroxyl)carbamate (93.1 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [4:6 (v/v)] to afford the title compound **2c** as an off-white solid and a mixture of **2c** and **2c'** as a yellow solid (**2c**:**2c'**=3:1, 80.5 mg, 0.240 mmol, 80% yield).

2c: R_f = 0.50 EtOAc:Hexanes [7:3 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.07 (s, 1.H), 7.80 (s, 1H), 7.45 (q, *J* = 6.8 Hz, 1H), 7.31 (td, *J* = 8.6, 1.9 Hz, 1H), 7.12 (td, *J* = 8.6 2.3 Hz, 1H), 3.91 (s, 3H), 3.82 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 161.85 (dd, *J* = 12.1, 246.8 Hz), 159.54 (dd, *J* = 12.2, 248.1 Hz), 157.34, 150.22, 149.86, 141.39, 133.07 (q, *J* = 4.6 Hz), 125.16, 120.76 (q, *J* = 6.4 Hz), 114.8, 111.51 (q, *J* = 8.2 Hz), 108.93, 104.04 (t, *J* =26.2 Hz), 54.05, 53.90. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$, 25 ºC) δ -111.97 (q, *J* = 8.8 Hz, 1F), -113.05 (m, 1F). **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{11}F_2N_3O_4Na$ $[(M + Na)^+]$, 358.0610, found, 358.0615.

A mixture of 2c and 2c': R_f = 0.60, 0.50 EtOAc:Hexanes [7:3 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.08 (s, 1.06H, **2c**), 11.66 (s, 0.93H, **2c'**), 8.38 (s, 0.86H, **2c'**), 7.80 (s, 1H, **2c**), 7.46 (m, 1.97H, **2c** and **2c'**), 7.33 (m, 2.01H, **2c** and **2c'**), 7.16 (m, 2.05H, **2c** and **2c'**), 3.95 (s, 2.68H, **2c'**), 3.91 (s, 3.08H, **2c**), 3.82 (s, 2.97H, **2c**), 3.79 (s, 2.82H, **2c'**). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 162.45 (dd, *J* =12.1, 247.0 Hz), 161.85 (dd, *J* =12.1, 246.7 Hz), 160.03 (dd, *J* =12.5, 248.4 Hz), 159.54 (dd, *J* =12.6, 248.2 Hz), 157.34, 156.99, 150.45, 149.86, 141.39, 137.31, 133.64 9 (dd, *J* = 4.9, 10.2 Hz), 133.07 (dd, *J* = 3.8, 9.0 Hz), 129.35, 125.16, 120.76 (dd, *J* = 3.5, 15.6 Hz), 120.67, 115.24 (d, *J* = 19.5 Hz), 114.83, 111.60 (m), 108.94, 104.19 (m), 98.05, 54.06, 53.99, 53.90, 53.67. **^{19}F NMR** (376 MHz, $(CD_3)_2SO$, 25 ºC) δ -110.74 (q, *J* = 8.9 Hz, 0.87F, **2c'**), -111.96 (quint, *J* = 8.9 Hz, 1F, **2c**), -112.18 (quint, J = 7.8 Hz, 0.81F, **2c'**), -113.01 (quint, J = 8.0 Hz, 1F, **2c**). Due to the poor solubility of the products in organic solvents, the minor isomer **2c'** was eluted together with the major isomer **2c**.

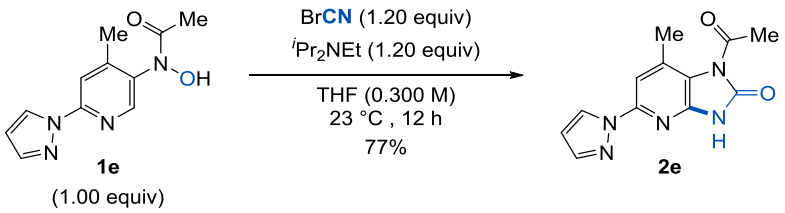
1-Acetyl-5-methoxy-7-methyl-1*H*-imidazo[4,5-*b*]pyridine-2(3*H*)-one (2d)



The reaction was performed according to the general procedure A using *N*-hydroxy-*N*-(6-methoxy-4-methylpyridin-3-yl)acetamide (117.7 mg, 0.600 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was concentrated *in vacuo*, and it was washed with H_2O (3 × 1.00 mL) and hexane (1.00 mL) to afford the title compound as a brown solid (127.4 mg, 0.576 mmol, 96% yield).

2d: ^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 11.87 (s, 1H), 6.33 (s, 1H), 3.80 (s, 3H), 2.60 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 169.50, 160.89, 152.37, 142.55, 137.62, 114.15, 104.56, 53.57, 25.75, 21.26. **HRMS** (ESI-TOF) *m/z* calcd for $C_{10}H_{10}N_3O_3$ $[(M - H)^-]$, 220.0728, found, 220.0729.

1-Acetyl-7-methyl-5-(1*H*-pyrazol-1-yl)-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (2e)

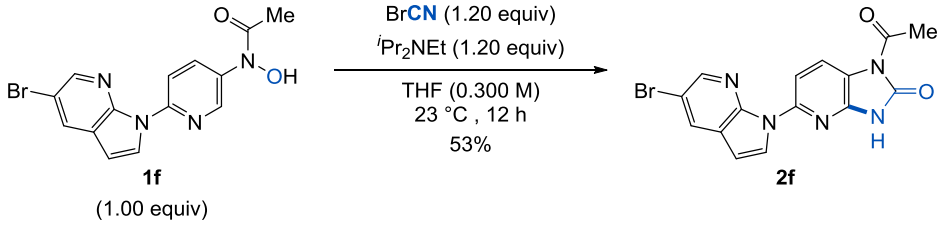


The reaction was performed according to the general procedure A using *N*-hydroxy-*N*-(4-methyl-6-(1*H*-pyrazol-1-yl)pyridin-3-yl)acetamide (69.7 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [4:6 (v/v)] to afford the title compound as an off-white solid (59.4 mg, 0.231 mmol, 77% yield).

R$_f$ = 0.63 EtOAc:Hexanes [7:3 (v/v)].

2e: ^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.17 (s, 1H), 8.40 (d, *J* = 2.0 Hz, 1H), 7.78 (s, 1H), 7.45 (s, 1H), 6.55 (s, 1H), 2.64 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 169.49, 152.40, 146.44, 143.66, 141.91, 136.46, 126.76, 118.58, 108.05, 107.81, 25.83, 21.48. **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{12}N_5O_2$ [$(M + H)^+$], 258.0986, found, 258.0988.

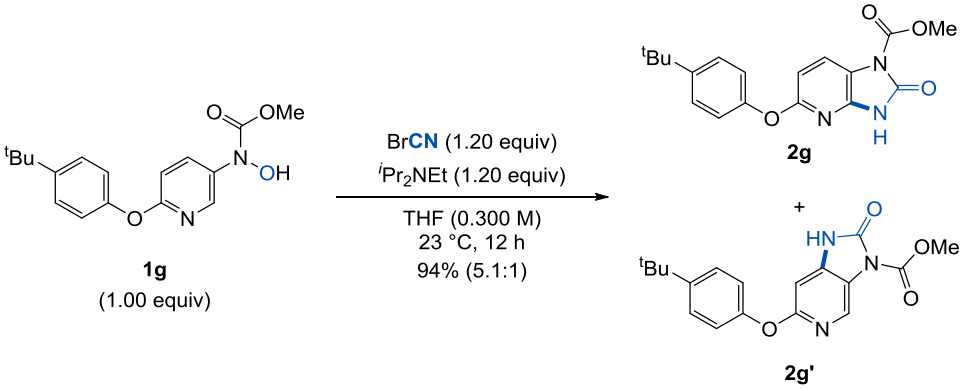
1-Acetyl-5-(5-bromo-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (2f)



The reaction was performed according to the general procedure A using *N*-(6-(5-bromo-1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)pyridin-3-yl)-*N*-hydroxyacetamide (104.2 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was concentrated *in vacuo*, and it was washed with H_2O (3 × 1.00 mL) and hexane (1.00 mL) to afford the title compound as a yellow solid (59.2 mg, 0.159 mmol, 53% yield).

2f: ^{1}H NMR (700 MHz, $(CD_3)_2SO$, 50 ºC) δ 12.17 (s, 1H), 8.47 (s, 1H), 8.36 (s, 3H), 8.26 (s, 1H), 6.76 (s, 1H), 2.64 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 58 ºC) δ 170.39, 152.37, 145.59, 145.07, 143.77, 143.50, 131.96, 128.59, 124.83, 123.99, 119.70, 113.08, 108.85, 102.70, 25.45. **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{11}BrN_5O_2$ [$(M + H)^+$], 372.0091, found, 372.0095.

Methyl 5-(4-(*tert*-butyl)phenoxy)-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridine-1-carboxylate (2g) and methyl 6-(4-(*tert*-butyl)phenoxy)-2-oxo-1*H*-imidazo[4,5-*c*]pyridine-3(2*H*)-carboxylate (2g')

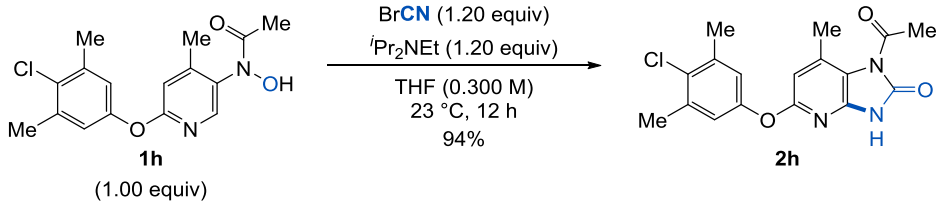


The reaction was performed according to the general procedure A using methyl (6-(4-(*tert*-butyl)phenoxy)pyridine-3-yl)(hydroxyl)carbamate (100.0 mg, 0.316 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [4:6 to 7:3 (v/v)] to afford the title compound **2g** as a white solid and **2g'** as an off-white solid. (**2g**:**2g'** = 5.1:1, 101.6 mg, 0.298 mmol, 94% yield).

2g: $\mathbf{R_f}$ = 0.54 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (500 MHz, $(CD_3)_2SO$, 25 ºC) δ 11.93 (br. s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 2.0, 6.7 Hz, 2H), 7.02 (dd, *J* = 2.0, 6.7 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (125 MHz, $(CD_3)_2SO$, 25 ºC) δ 159.32, 152.14, 150.22, 149.71, 146.60, 141.79, 126.45, 124.53, 120.03, 116.68, 103.47, 53.89, 34.12, 31.25. **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{20}N_3O_4$ [$(M + H)^+$], 342.1448, found, 342.1446.

2g': $\mathbf{R_f}$ = 0.36 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 11.75 (br. s, 1H), 8.29 (s, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.56 (s, 1H), 3.92 (s, 3H), 1.29 (s, 9H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 159.53, 151.93, 150.15, 150.09, 146.64, 138.95, 130.45, 126.38, 121.62, 120.44, 91.50, 53.98, 34.15, 31.28.

1-Acetyl-5-(4-chloro-3,5-dimethylphenoxy)-7-methyl-1*H*-imidazo[4,5-*b*]pyridine-2(3*H*)-one (2h)

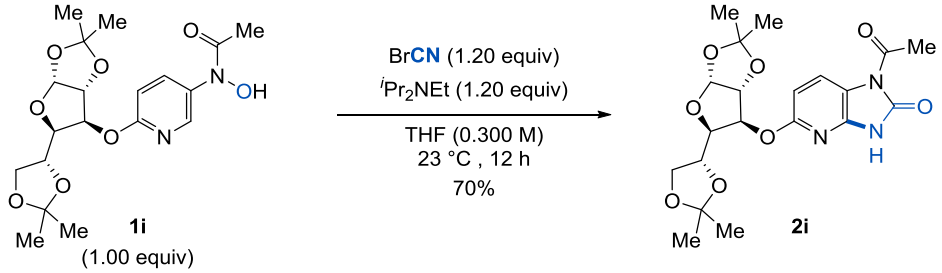


The reaction was performed according to the general procedure A using *N*-(6-(4-chloro-3,5-dimethylphenoxy)-4-methylpyridin-3-yl)-*N*-hydroxyacetamide (101.0 mg, 0.300 mmol, 1.00 equiv) as the

substrate. After 12 h, the reaction mixture was concentrated *in vacuo*, and it was washed with H_2O (3 × 1.00 mL) and hexane (1.00 mL) to afford the title compound as an off-white solid (102.0 mg, 0.282 mmol, 94% yield).

2h: **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 9.18 (s, 1H), 6.82 (a, 2H), 6.38 (s, 1H), 2.74 (s, 3H), 2.40 (s, 3H), 2.32 (s, 6H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 169.83, 160.52, 152.29, 152.20, 142.10, 139.42, 137.56, 130.51, 120.55, 116.46, 107.59, 26.25, 22.16, 20.99. **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{17}ClN_3O_3$ [(M + H)$^+$], 346.0953, found, 346.0958.

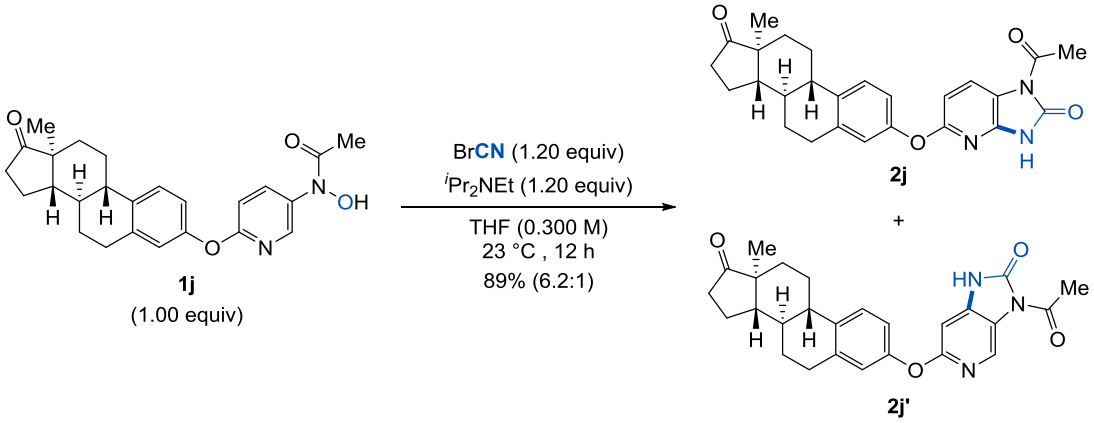
1-Acetyl-5-(((3*aR*,5*R*,6*S*,6*aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (2i)



The reaction was performed according to the general procedure A using *N*-(6-(((3a*R*,5*R*,6*S*,6a*R*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl)oxy)pyridine-3-yl)-*N*-hydroxyacetamide (127.9 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was concentrated *in vacuo* and purified by preparative TLC (thickness: 1 mm) using EtOAc:Hexanes (7:3 (v/v)) (prep TLC was developed twice) and EtOAc:hexanes (1:1 (v/v)) for development. The purification afforded the title compound as clear solid (94.3 mg, 0.209 mmol, 70% yield).

2i: **R_f** = 0.45 EtOAc:Hexanes [3:7 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 12.20 (s, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 6.37 (d, *J* = 8.5 Hz, 1H), 5.90 (d, *J* = 3.6 Hz, 1H), 5.46 (d, *J* = 3.0 Hz, 1H), 4.62 (m, 1H), 4.59 (d, *J* = 3.6 Hz, 1H), 4.34 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.21 (m, 2H), 2.67 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.39 (s, 3H), 1.25 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 169.85, 159.19, 151.48, 140.15, 125.69, 115.51, 112.10, 110.02, 105.33, 103.38, 83.16, 79.74, 78.20, 72.64, 67.33, 27.25, 27.00, 26.23, 25.34, 25.28. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{26}N_3O_8$ [(M + H)$^+$], 436.1714, found, 436.1719.

1-Acetyl-5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (2j) and 3-acetyl-6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-1*H*-imidazo[4,5-*c*]pyridin-2(3*H*)-one (2j')



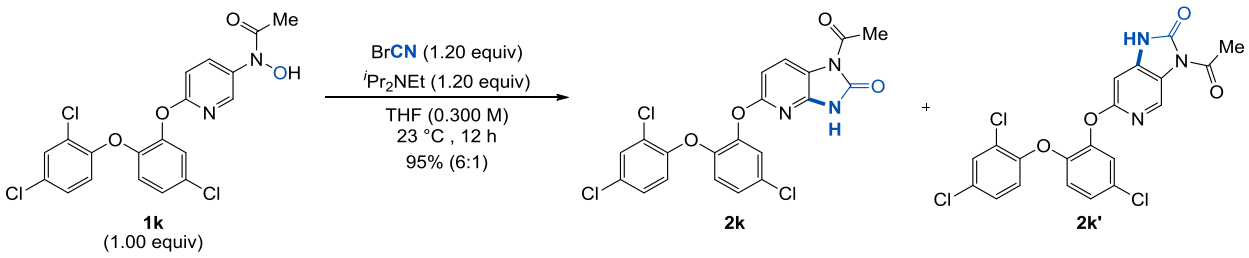
The reaction was performed according to the general procedure A using *N*-hydroxy-*N*-(6-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pyridin-3-yl)acetamide (121.9 mg, 0.290 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [2:8 to 1:0 (v/v)] to afford the title compound **2j** and the mixture of the title compound **2j** and **2j'** as an off-white solid (**2j**:**2j'**=6.2:1, 115.2 mg, 0.258 mmol, 89% yield).

2j: $\mathbf{R}_f$ = 0.52 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.00 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 2.83 (m, 2H), 2.58 (s, 3H), 2.45 (m, 1H), 2.38 (m, 1H), 2.25 (m, 1H), 2.07 (m, 1H), 1.96 (m, 2H), 1.78 (m, 1H), 1.55 (m, 3H), 1.41 (m, 3H), 0.85 (s, 3H). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 219.64, 169.91, 159.51, 152.30, 151.75, 142.24, 138.07, 135.75, 126.64, 125.32, 120.41, 117.96, 116.93, 103.53, 49.59, 47.31, 43.55, 37.59, 35.38, 31.34, 28.94, 25.86, 25.39, 25.08, 21.13, 13.53. **HRMS** (ESI-TOF) m/z calcd for $C_{26}H_{28}N_3O_4$ [$(M + H)^+$], 446.2074, found, 446.2078.

A mixture of 2j and 2j': $\mathbf{R}_f$ = 0.52, 0.38 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 11.99 (br, 1.23H, **2j** and **2j'**), 8.52 (s, 0.19H, **2j'**), 8.18 (d, *J* = 8.4 Hz, 1H, **2j**), 7.30 (d, *J* = 8.5 Hz, 1.16H, **2j** and **2j'**), 6.84 (m, 1.24H, **2j** and **2j'**), 6.80 (m, 1.26H, **2j** and **2j'**), 6.65 (d, *J* = 8.4 Hz, 0.99H, **2j**), 6.57 (s, 0.20H, **2j'**), 2.83 (m, 2.75H, **2j** and **2j'**), 2.58 (s, 0.76H, **2j'**), 2.57 (s, 3H, **2j**), 2.45 (m, 1.27H, **2j** and **2j'**), 2.38 (m, 1.27H, **2j** and **2j'**), 2.25 (m, 1.38H, **2j** and **2j'**), 2.07 (m, 1.50H, **2j** and **2j'**), 1.96 (m, 2.91H, **2j** and **2j'**), 1.77 (m, 1.35H, **2j** and **2j'**), 1.56 (m, 3.84H, **2j** and **2j'**), 1.40 (m, 3.79H, **2j** and **2j'**) 0.85 (s, 4.33H, **2j** and **2j'**). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 219.64,169.91, 169.63, 159.65, 159.52, 152.30, 152.10, 152.06, 151.75, 142.22, 139.19, 138.07, 137.94, 135.76, 131.24, 126.65, 126.52, 125.33,

120.71, 120.42, 118.24, 117.97, 116.93, 103.53, 91.63, 49.60, 47.31, 43.56, 37.61, 35.39, 31.36, 28.95, 25.88, 25.40, 25.09, 21.15, 13.54. Due to the poor solubility of the products in organic solvents, the minor isomer **2j'** was eluted together with the major isomer **2j**.

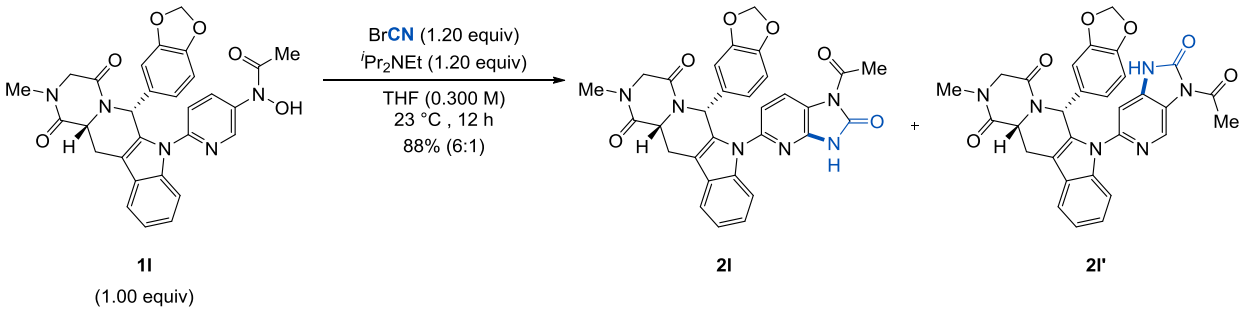
1-Acetyl-5-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)-1,3-dihydro-2*H*-imidazo[4,5-*b*]pyridin-2-one (2k) and 3-Acetyl-6-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)-1,3-dihydro-2*H*-imidazo[4,5-*c*]pyridin-2-one (2k')



The reaction was performed according to the general procedure A using *N*-(6-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)pyridin-3-yl)-*N*-hydroxyacetamide (101 mg, 0.230 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with ^{i}PrOH:DCM [1:100 to 1:30 (v/v)] to afford the title compound **2k** as a white solid and a mixture of **2k** and **2k'** as a white solid (**2k**:**2k'**=6:1, 101.5 mg, 0.218 mmol, 95% yield).

R$_f$ =0.85, 0.73 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$) δ 11.99 (s, 1.05H, **2k** and **2k'**), 9.59 (s, 0.19H, **2k'**), 8.45 (s, 0.16H, **2k'**), 8.15 (d, *J* = 8.5 Hz, 0.88H, **2k**), 7.92 (s, 0.20H, **2k'**), 7.65 (s, 0.97H, **2k**), 7.58 (s, 0.11H, **2k'**), 7.50 (s, 0.82H, **2k**), 7.46 (d, *J* = 2.3 Hz, 0.16H, **2k'**), 7.33 (d, *J* = 8.8 Hz, 2.0H, **2k**), 7.12 (d, *J* = 8.8 Hz, 1.02H, **2k**), 6.97 (d, *J* = 8.8 Hz, 0.86H, **2k**), 6.95 (d, *J* = 8.8 Hz, 0.22H, **2k'**), 6.63 (d, *J* = 8.5 Hz, 0.86H, **2k**), 6.56 (s, 0.15H, **2k'**), 2.56 (s, 3.10H, **2k and 2k'**).**^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 170.38, 158.84, 152.11, 151.13, 146.85 , 145.36, 142.28, 130.36, 129.15, 129.00 , 128.50, 126.68, 125.90, 124.82, 124.51, 122.1,120.58, 117.65 ,103.14 ,25.56. **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{13}Cl_3N_3O_4$ [$(M + H)^+$], 463.9966, found, 463.9973. Due to similar R$_f$, the major and minor isomers were eluted together.

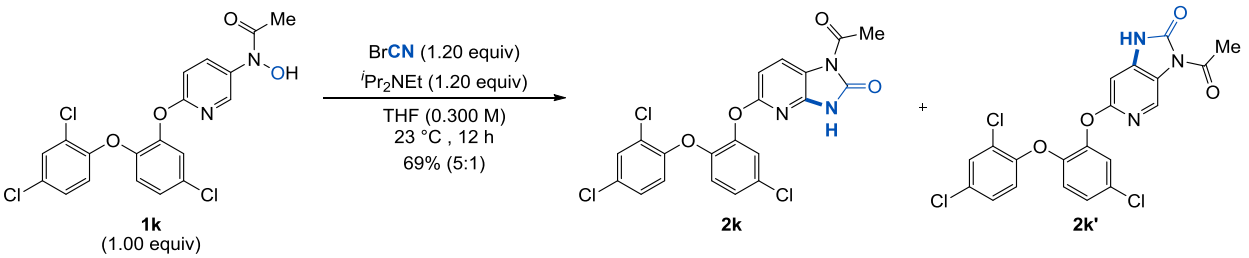
(6*R*,12*aR*)-7-(1-acetyl-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridine-5-yl)-6-(benzo[*d*][1,3]dioxol-5-yl)-2-methyl-2,3,6,7,12,12*a*-hexahydropyrazino[1',2':1,6]pyrido[3,4-*b*]indole-1,4-dione (2l) and (6*R*,12*a*R)-7-(3-acetyl-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*c*]pyridine-6-yl)-6-(benzo[*d*][1,3]dioxol-5-yl)-2-methyl-2,3,6,7,12,12*a*-hexahydropyrazino[1',2':1,6]pyrido[3,4-*b*]indole-1,4-dione (2l')



The reaction was performed according to the general procedure A using *N*-(6-((6*R*,12*aR*)-6-(benzo[*d*][1,3]dioxol-5-yl)-2-methyl-1,4-dioxo-1,3,4,6,12,12*a*-hexahydropyrazino[1',2':1,6]pyrido[3,4-*b*]indol-7(2*H*)-yl)pyridin-3-yl)-*N*-hydroxyacetamide (161 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 12 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:DCM [1:200 to 1:10 (v/v)] to afford the title compound **2l** as a white solid and a mixture of **2l** and **2l'** as a white solid (**2l**:**2l'**=6:1, 99.4 mg, 0.264 mmol, 88% yield). Product contained <5% of inseparable impurity.

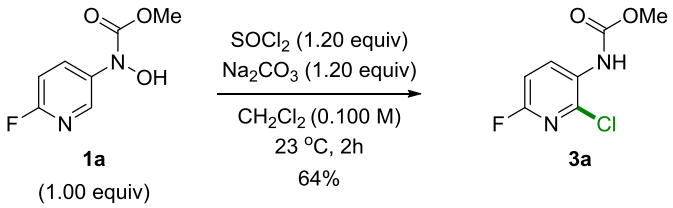
A mixture of 2l and 2l': R_f = 0.60, 0.66 ^{i}PrOH:DCM [1:9 (v/v)]. **^{1}H NMR** (700 MHz, $(CD_3)_2SO$, 25 ºC) δ 12.34 (s, 0.76H, **2l'**), 12.00 (s, 0.23H, **2l'**), 9.01 (s, 0.22H, **2l'**), 8.27 (d, *J* = 8.1 Hz, 0.83H, **2l'**), 7.73 (d, *J* = 3.1 Hz, 0.83H, **2l'**), 7.31 (d, *J* = 3.8 Hz, 1H, **2l**), 7.30 (d, *J* = 3.2 Hz, 0.86H, **2l**), 7.17 (s, 1.6H, **2l** and **2l'**) 6.98 (d, *J* = 8.1 Hz, 0.64H, **2l'**), 6.53 (s, 0.62 H, **2l'**), 6.50 (d, *J* = 8.1 Hz, 0.71H, **2l'**), 6.29 (d, *J* = 1.3 Hz, 0.77 H, **2l'**), 6.17 (dd, *J* = 1.4, 8.2 Hz, 0.82H, **2l**), 5.82 (d, *J* = 2.4 Hz, 1.7H, **2l** and **2l'**), 4.53 (dd, *J* = 11.6, 3.9 Hz, 0.96 H **2l**), 4.34 (s, 0.67H, **2l'**) 4.18 (d, *J* = 17.1 Hz, 1.04H **2l** and **2l'**), 4.02 (q, *J* = 7.1 Hz, 1.4H, **2l** and **2l'**) , 3.93 (d, *J* = 17.0 Hz, 1H, **2l**), 3.76 (d, *J* = 4.2 Hz, 0.54H, **2l'**), 3.66 (dd, *J* = 16.0, 4.5 Hz, 0.99H, **2l**), 2.91 (s, 2.3H, **2l** and **2l'**), 2.65 (s, 2.1H, **2l** and **2l'**), 1.98 (s, 2.1H, **2l** and **2l'**), 1.16 (s, 3H, **2l** and **2l'**), 1.03 (d, *J* = 6.1 Hz, 2.8H, **2l** and **2l'**). **^{13}C NMR** (175 MHz, $(CD_3)_2SO$, 25 ºC) δ 170.72, 167.22, 166.76, 152.43, 147.22, 146.44, 144.51, 144.22, 137.27, 135.77, 134.93, 126.36, 123.89, 123.42, 121.26, 121.11, 120.75, 119.39, 114.23, 110.80, 109.48, 107.98, 107.52, 101.28, 55.43, 54.85, 51.84, 33.29, 25.72, 23.84. **HRMS** (ESI-TOF) *m/z* calcd for $C_{30}H_{25}N_6O_6$ [$(M + H)^+$], 565.1830, found, 565.1841. Due to similar R_f, the major and minor isomers were eluted together.

Large-scale synthesis of 1-acetyl-5-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)-1,3-dihydro-2*H*-imidazo[4,5-*b*]pyridin-2-one (2k) and 3-Acetyl-6-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)-1,3-dihydro-2*H*-imidazo[4,5-*c*]pyridin-2-one (2k')



In a glovebox, to an oven-dried 20 mL screw cap vial were added *N*-(6-(5-chloro-2-(2,4-dichlorophenoxy)phenoxy)pyridin-3-yl)-*N*-hydroxyacetamide (1.06 g, 2.40 mmol, 1.00 equiv), *N*,*N*-diisopropylethylamine ($^{i}Pr_2NEt$) (502 µL, 372 mg, 2.88 mmol, 1.20 equiv) and THF (4.00 mL) with a magnetic stir bar. Cyanogen bromide (305 mg, 2.88 mmol, 1.20 equiv) solution in THF (4.00 mL) was prepared separately. The reaction vials were then capped and taken out of the glovebox. The substrate solution was placed in an ice bath. To this suspension were added cyanogen bromide (38.1 mg, 0.360 mmol, 1.20 equiv). After the reaction mixture was warmed up to 23 °C, it was stirred for 12 h and then concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with EtOAc:Hexanes [2:8 to 3:7 (v/v)] to afford the title compound mixture of **2k** and **2k'** as a white solid (**2k**:**2k'**=6.8:1, 988 mg, 2.14 mmol, 89% yield).

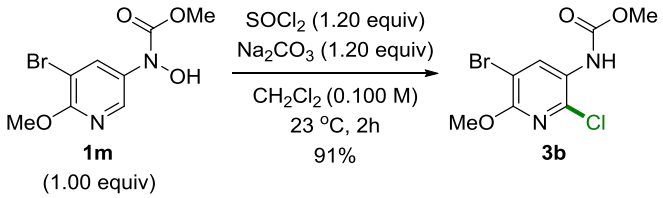
Methyl (2-chloro-6-fluoropyridin-3-yl)carbamate (3a)



The reaction was performed according to the general procedure B using methyl (6-fluoropyridin-3-yl)(hydroxy)carbamate (100 mg, 0.537 mmol, 1.00 equiv) as the substrate. After 2 h, the reaction mixture was purified by preparative TLC, eluting with EtOAc:Hexanes [1:4 (v/v)] to afford the title compound as a white solid (69.9 mg, 0.342 mmol, 64% yield).

$\mathbf{R_f}$ = 0.47 EtOAc:Hexanes [1:4 (v/v)].**^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.58 (br. s, 1H), 7.03 (br. s, 1H), 6.90 (dd, *J* = 9.03, 3.44 Hz, 1H), 3.80 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 156.9 (d, *J* = 243.3 Hz), 153.6, 135.5, 132.9, 130.0 (d, *J* = 4.8 Hz), 108.8 (d, *J* = 36.3 Hz), 53.1. **^{19}F NMR** (376 MHz, $CDCl_3$, 25 ºC) δ – 73.8 (s). **HRMS** (ESI-TOF) (m/z): calcd for $C_7H_6ClFN_2O_2$ ($[M + H]^+$), 205.0715, found, 205.0716.

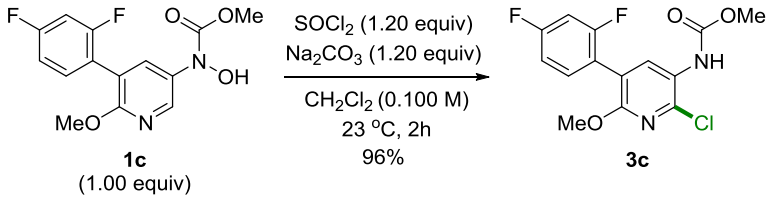
Methyl (5-bromo-2-chloro-6-methoxypyridin-3-yl)carbamate (3b)



The reaction was performed according to the general procedure B using methyl (5-bromo-6-methoxypyridin-3-yl)(hydroxy)carbamate (100 mg, 0.361 mmol, 1.00 equiv) as the substrate. After 2 h, the reaction mixture was purified flash column chromatography, eluting with EtOAc:Hexanes [1:9 (v/v)] to afford the title compound as a white solid (97.3 mg, 0.329 mmol, 91% yield).

$\mathbf{R_f}$ = 0.58 EtOAc:Hexanes [1:4 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.65 (br. s, 1H), 6.81 (br. s, 1H), 3.98 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 155.1, 153.7, 134.6, 134.4, 126.2, 105.4, 55.3, 53.0. **HRMS** (ESI-TOF) (m/z): calcd for $C_8H_8BrClN_2O_3$ ($[M + H]^+$), 294.9480, found, 294.9483.

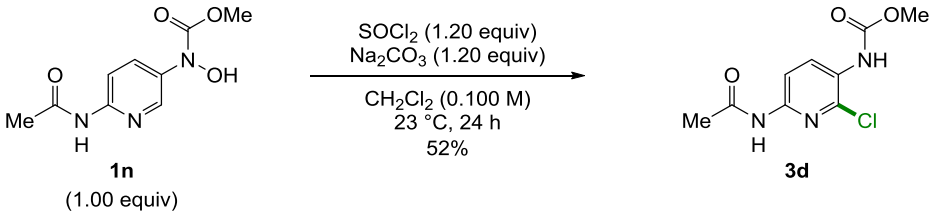
Methyl (2-chloro-5-(2, 4-difluorophenyl)-6-methoxypyridin-3-yl)carbamate (3c)



The reaction was performed according to the general procedure B using methyl (5-(2, 4-difluorophenyl)-6-methoxypyridin-3-yl)(hydroxy)carbamate (100 mg, 0.322 mmol, 1.00 equiv) as the substrate. After 2 h, the reaction mixture was purified flash column chromatography, eluting with EtOAc:Hexanes [1:9 to 1:4 (v/v)] to afford the title compound as a white solid (102 mg, 0.310 mmol, 96% yield).

R_f = 0.60 (EtOAc:Hexanes [1:4 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.36 (br. s, 1H), 7.35 (td, *J* = 8.50, 6.24 Hz, 1H), 6.93 (td, *J* = 8.28, 2.80 Hz, 1H), 6.91–6.82 (m, 2H), 3.92 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 161.6 (d, *J* = 249.1 Hz), 161.6 (d, *J* = 249.7 Hz), 156.1, 154.0, 135.7, 133.3, 132.5 (q, *J* = 4.7 Hz), 125.5, 119.4 (dd, *J* =15.1, 3.7 Hz), 117.6, 111.4 (dd, *J* = 20.5, 3.1 Hz), 104.3 (t, *J* = 25.5 Hz), 54.6, 52.9. **^{19}F NMR** (376 MHz, $CDCl_3$, 25 ºC) δ –110.0 (s), –110.3 (s). **HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{11}ClF_2N_2O_3$ ($[M + H]^+$), 329.0499, found, 329.05.

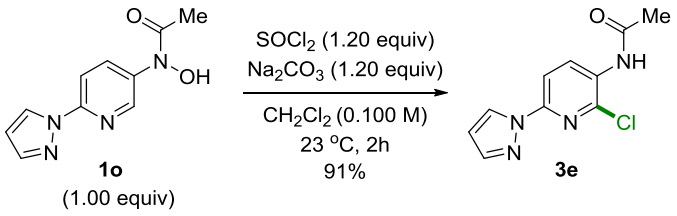
***N,N'*-(6-Chloropyridine-2,5-diyl)diacetamide (3d)**



The reaction was performed according to the general procedure B using *N*-(6-acetamidopyridin-3-yl)-*N*-hydroxyacetamide (105 mg, 0.500 mmol, 1.00 equiv) as the substrate. After 24 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:hexanes [1:4 to 1:1 (v/v)] to afford the title compound as an off white solid (59.0 mg, 0.260 mmol, 52% yield).

R_f = 0.58 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.46 (s, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 7.80 (s, 1H), 6.96 (s, 1H), 3.81 (s, 3H), 2.18 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 168.22, 153.58, 145.59, 137.17, 130.68, 128.08, 113.21, 52.88, 24.58. **HRMS** (ESI-TOF) *m/z* calcd for $C_9H_{10}ClN_3O_3$ [$(M + H)^+$], 244.0483, found, 244.0482.

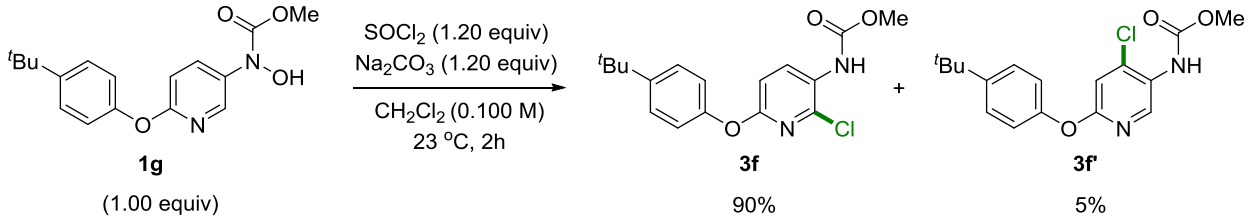
_N_-(2-Chloro-6-(1_H_-pyrazol-1-yl)pyridin-3-yl)acetamide (3e)



The reaction was performed according to the general procedure B using *N*-(6-(1*H*-pyrazol-1-yl)pyridin-3-yl)-*N*-hydroxyacetamide (100 mg, 0.458 mmol, 1.00 equiv) as the substrate. After 2h, the reaction mixture was purified flash column chromatography, eluting with EtOAc:Hexanes [3:7 to 1:4 (v/v)] to afford the title compound as an off-white solid (98.5 mg, 0.416 mmol, 91% yield).

R_f = 0.45 EtOAc:Hexanes [3:2 (v/v)] **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.83 (d, *J* = 8.60 Hz, 1H), 8.44 (d, *J* = 3.01 Hz, 1H), 7.91 (d, *J* = 8.60 Hz, 1H), 7.72 (d, *J* = 1.29 Hz, 1H), 7.56 (br. s, 1H), 6.45 (t, *J* = 2.37 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 168.5, 146.2, 142.5, 137.3, 132.2, 129.7, 127.2, 111.8, 108.2, 25.0. **HRMS** (ESI-TOF) (m/z): calcd for $C_{10}H_9ClN_4O$ ($[M + H]^+$), 237.0538, found, 237.0535.

Methyl (6-(4-(*tert*-butyl)phenoxy)-2-chloropyridin-3-yl)carbamate (3f) and methyl (6-(4-(*tert*-butyl)phenoxy)-4-chloropyridin-3-yl)carbamate (3f')

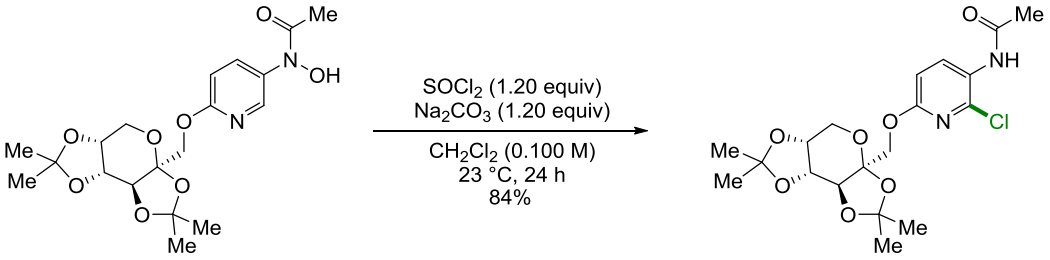


The reaction was performed according to the general procedure B using (6-(4-(*tert*-butyl)phenoxy)pyridin-3-yl)(hydroxy)carbamate (100 mg, 0.316 mmol, 1.00 equiv) as the substrate. After 2h, the reaction mixture was purified by preparative TLC, eluting with EtOAc:Hexanes [9:1(v/v)] to afford the title compounds **3f** (94.9 mg, 0.283 mmol, 90% yield) and **3f'** (5.00 mg, 0.015 mmol, 5% yield) as off-white solids.

3f: R_f = 0.46 EtOAc:Hexanes [4:4 (v/v)] **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.42 (br. s, 1H), 7.39 (d, *J* = 8.60 Hz, 2H), 7.04 (d, *J* = 9.03 Hz, 2H), 6.94 (br. s, 1H), 6.78 (d, *J* = 9.03 Hz, 1H), 3.81 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 158.1, 153.9, 151.8, 147.8, 136.5, 132.1, 127.3, 126.8, 120.0, 110.4, 52.9, 34.6, 31.6. **HRMS** (ESI-TOF) (m/z): calcd for $C_{17}H_{19}ClN_2O_3$ ($[M + H]^+$), 335.1157, found, 335.1155.

3f': R_f = 0.30 EtOAc:Hexanes [1:4 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.16 (br. s, 1H), 7.90 (d, *J* = 2.58 Hz, 1H), 7.40 (d, *J* = 9.03 Hz, 2H), 7.05 (d, *J* = 9.04 Hz, 2H), 6.56 (br. s, 1H), 3.79 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 155.4, 154.1, 151.7, 147.6, 135.5, 130.8, 126.6, 120.3, 119.6, 111.4, 53.0, 34.6, 31.6. **HRMS** (ESI-TOF) (m/z): calcd for $C_9H_9NO_2F_3$ ([M + H]$^+$), 220.0585, found, 220.0583.

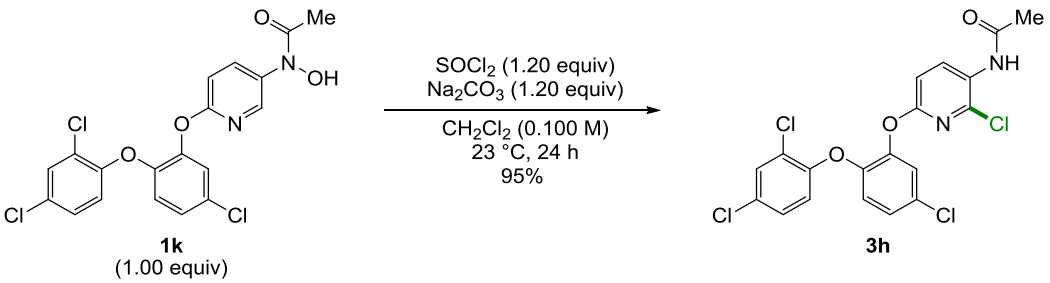
***N*-(2-Chloro-6-(((3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methoxy)pyridin-3-yl)acetamide (3g)**



The reaction was performed according to the general procedure B using *N*-hydroxy-*N*-(6-(((3*aS*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-3*aH*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3*a*-yl)methoxy)pyridin-3-yl)acetamide (123 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 24 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [1:4 to 1:1 (v/v)] to afford the title compound as a brown solid (129 mg, 0.252 mmol, 84% yield).

R_f = 0.45 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.50 (d, *J* = 8.8 Hz, 1H), 7.35 (s, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 4.61 (q, *J* = 7.5 Hz, 2H), 4.43 (d, *J* = 2.2 Hz, 1H), 4.27 (q, *J* = 11.2 Hz, 2H), 3.94 (d, *J* = 13.0 Hz, 1H), 3.79 (d, *J* = 13.0 Hz, 1H), 2.22 (s, 3H), 1.54 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (175MHz, $CDCl_3$, 25 ºC) δ 163.56, 153.49, 131.50, 128.92, 120.96, 105.17, 104.38, 104.01, 97.27, 66.13, 65.74, 65.42, 62.60, 56.47 , 21.82, 21.77, 21.22, 21.17, 20.58, 20.52. **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{25}ClN_2O_7$ [(M + H)$^+$], 429.1423, found, 429.1418.

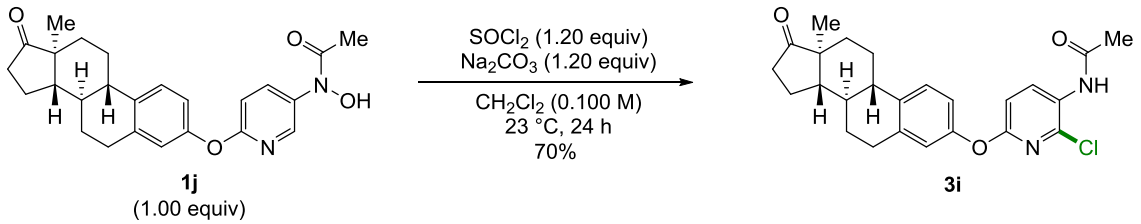
***N*-(2-Chloro-6-(5-chloro-2-(2, 4-dichlorophenoxy)phenoxy)pyridin-3-yl)acetamide (3h)**



The reaction was performed according to the general procedure B using *N*-(6-(5-chloro-2-(2, 4-dichlorophenoxy)phenoxy)pyridin-3-yl)-*N*-hydroxyacetamide (132 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 24 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:hexanes [1:4 to 1:1 (v/v)] to afford the title compound as an off white solid (125 mg, 0.285 mmol, 95% yield).

R_f = 0.65 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.63 (d, *J* = 8.8 Hz, 1H), 7.36 (s, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 1H), 7.17 (dd, *J* = 2.0, 8.7 Hz, 1H), 7.12 (dd, *J* = 2.0, 8.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.84 (q, *J* = 8.1 Hz, 2H), 2.22 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 168.30, 156.96, 150.96, 146.88, 144.46, 136.19, 133.63, 130.24, 129.53, 129.07, 127.91, 127.50, 126.27, 125.61, 124.19, 120.65, 120.11, 110.00, 24.72. **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{12}Cl_4N_2O_3$ [(M + H)$^+$], 456.9675, found, 456.9678.

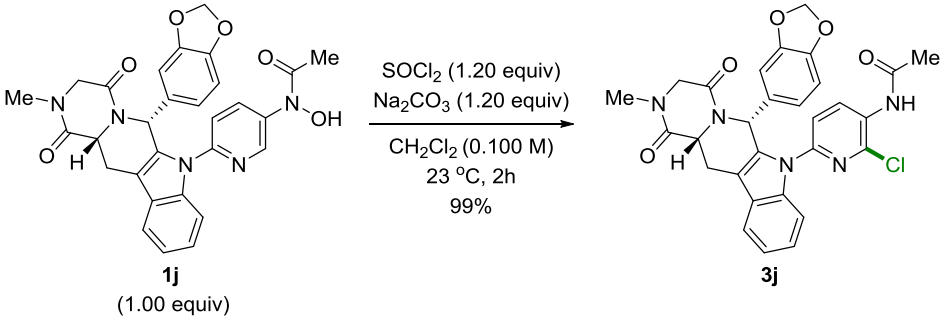
_N_-(2-Chloro-6-(((8*S*,9*S*,13*S*,14*S*)-9,13-dimethyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pyridine-3-yl)acetamide (3i)



The reaction was performed according to the general procedure B using *N*-(6-(((8*S*,9*S*,13*S*,14*S*)-9,13-dimethyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)pyridin-3-yl)-*N*-hydroxyacetamide (126 mg, 0.300 mmol, 1.00 equiv) as the substrate. After 24 h, the reaction mixture was purified by flash column chromatography on silica gel, eluting with EtOAc:Hexanes [1:4 to 1:1 (v/v)] to afford the title compound as an off white solid (91.0 mg, 0.210 mmol, 70% yield).

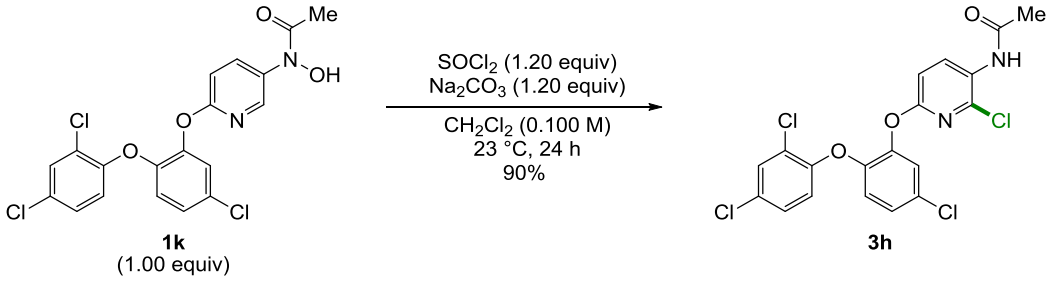
R_f = 0.45 EtOAc:Hexanes [1:1 (v/v)]. **^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.60 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.83 (s, 1H), 6.77 (d, *J* = 8.8 Hz, 1H), 2.89 (d, *J* = 9.6 Hz, 2H), 2.50 (dd, *J* = 8.7, 19.1 Hz, 1H), 2.41 (q, *J* = 5.3 Hz, 1H), 2.30 (t, *J* = 10.8 Hz, 1H), 2.24 (s, 3H), 2.14 (m, *J* = 9.3 Hz, 1H), 2.04 (m, *J* = 7.2 Hz, 2H), 1.97 (d, *J* = 12.6 Hz, 1H), 1.62 (m, *J* = 8.4 Hz, 2H), 1.53 (q, *J* = 9.1 Hz, 2H), 1.46 (t, *J* = 15.6 Hz, 2H), 0.92 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 220.86, 168.39, 158.38, 151.91, 138.37, 137.03, 136.43, 133.61, 126.98, 126.70, 120.58, 117.90, 110.11, 50.45, 47.99, 44.17, 38.09, 35.89, 31.58, 29.48, 26.40, 25.81, 24.70, 21.61, 13.87 **HRMS** (ESI-TOF) *m/z* calcd for $C_{25}H_{27}ClN_2O_3$ [(M + H)$^+$], 439.1783, found, 439.1781.

_N_-(6-((6_R_,12_aR_)-6-(Benzo[_d_][1,3]dioxol-5-yl)-2-methyl-1,4-dioxo-1,3,4,6,12,12a-hexahydropyrazino[1',2':1,6]pyrido[3,4-_b_]indol-7(2_H_)-yl)-2-chloropyridin-3-yl)acetamide (3j)



The reaction was performed according to the general procedure B using _N_-(6-((6_R_,12a_R_)-6-(benzo[_d_][1,3]dioxol-5-yl)-2-methyl-1,4-dioxo-1,3,4,6,12,12a-hexahydropyrazino[1',2':1,6]pyrido[3,4-_b_]indol-7(2_H_)-yl)pyridin-3-yl)-N-hydroxyacetamide (100 mg, 0.185 mmol, 1.00 equiv) as the substrate. After 2 h, the reaction mixture was purified flash column chromatography, eluting with EtOAc and then EtOH:MeOH [49:1 (v/v)] to afford the title compound as a yellow solid (102 mg, 0.183 mmol, 99% yield) $\mathbf{R}_f$ = 0.21, EtOAc.**^{1}H NMR** (700 MHz, $CDCl_3$, 25 ºC) δ 8.76 (d, _J_ = 8.60 Hz, 1H), 7.84 (s, 1H), 7.70–7.63 (m, 1H), 7.40–7.34 (m, 1H), 7.25–7.19 (m, 2H), 7.07 (d, _J_ = 8.60 Hz, 1H), 6.73 (s, 1H), 6.49 (s, 1H), 6.45–6.41 (m, 2H), 5.78 (dd, _J_ = 8.17, 0.86 Hz, 2H), 4.39–4.32 (m, 1H), 4.10 (d, _J_ = 17.21 Hz, 1H), 3.89 (d, _J_ = 17.64 Hz, 1H), 3.82 (dd, _J_ = 16.13, 4.52 Hz, 1H), 3.29–3.21 (m, 1H), 3.01 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (175 MHz, $CDCl_3$, 25 ºC) δ 168.9, 166.5, 166.4, 147.3, 146.8, 144.2, 138.0, 136.8, 134.3, 134.1, 131.3, 130.4, 126.6, 123.6, 121.8, 121.6, 119.1, 118.9, 110.4, 110.2, 108.3, 107.7, 101.1, 55.7, 55.6, 52.3, 33.6, 24.9, 23.9. **HRMS** (ESI-TOF) (m/z): calcd for $C_{29}H_{24}ClN_5O_5$ ([M + H]$^+$), 558.1539, found, 558.1538.

Large-Scale Synthesis of _N_-(2-Chloro-6-(5-chloro-2-(2, 4-dichlorophenoxy)phenoxy)pyridin-3-yl)acetamide (3h)



Under N_2 atmosphere, to a 50 mL flame-dried, septum capped RBF charged with a magnetic stir bar were added _N_-(6-(5-chloro-2-(2, 4-dichlorophenoxy)phenoxy)pyridin-3-yl)-_N_-hydroxyacetamide (1.10g, 2.50 mmol, 1.00 equiv), sodium carbonate (320 mg, 3.00 mmol, 1.20 equiv), and CH_2Cl_2 (25.00 mL, 0.100 M). Thionyl chloride (0.216 mL 3.00 mmol, 1.20 equiv) was then added to the suspension. After the reaction

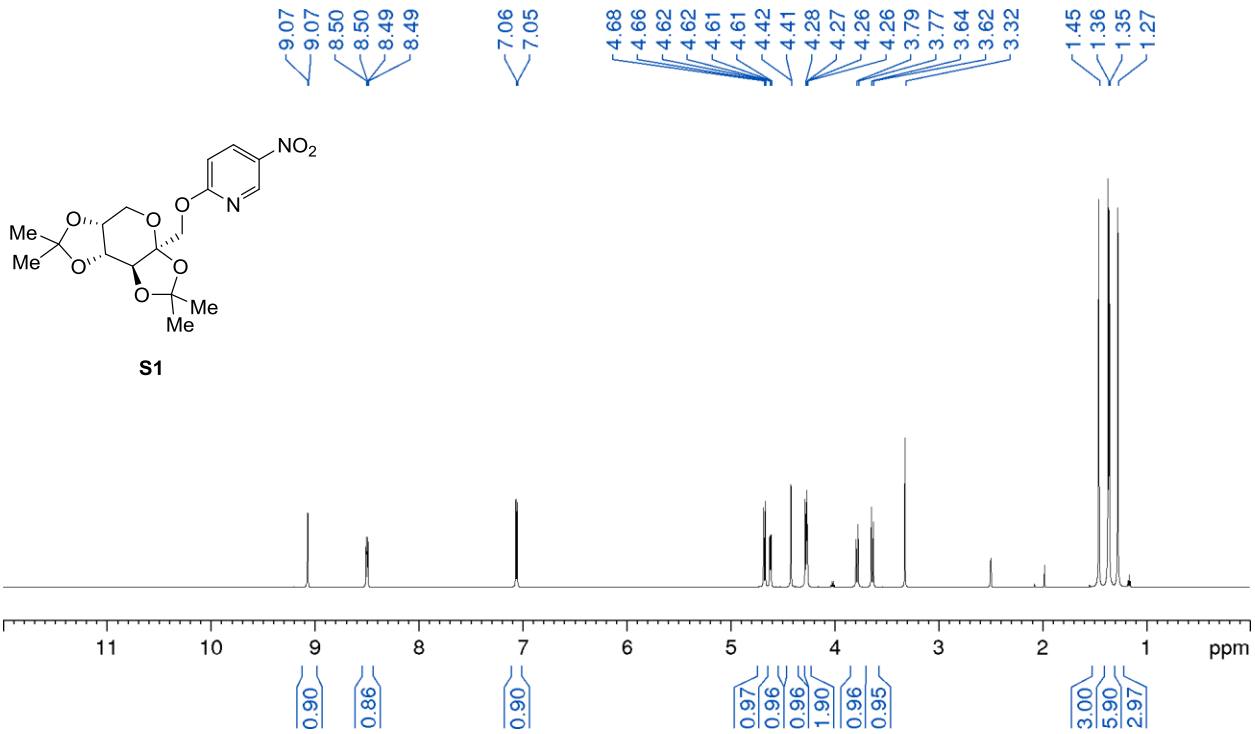
mixture was stirred at 23 °C for 24 h, it was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel, eluting with EtOAc:Hexanes [1:4 to 1:1 (v/v)] to afford the title compound as a white solid (1.03 g, 2.25 mol, 90% yield).

References:

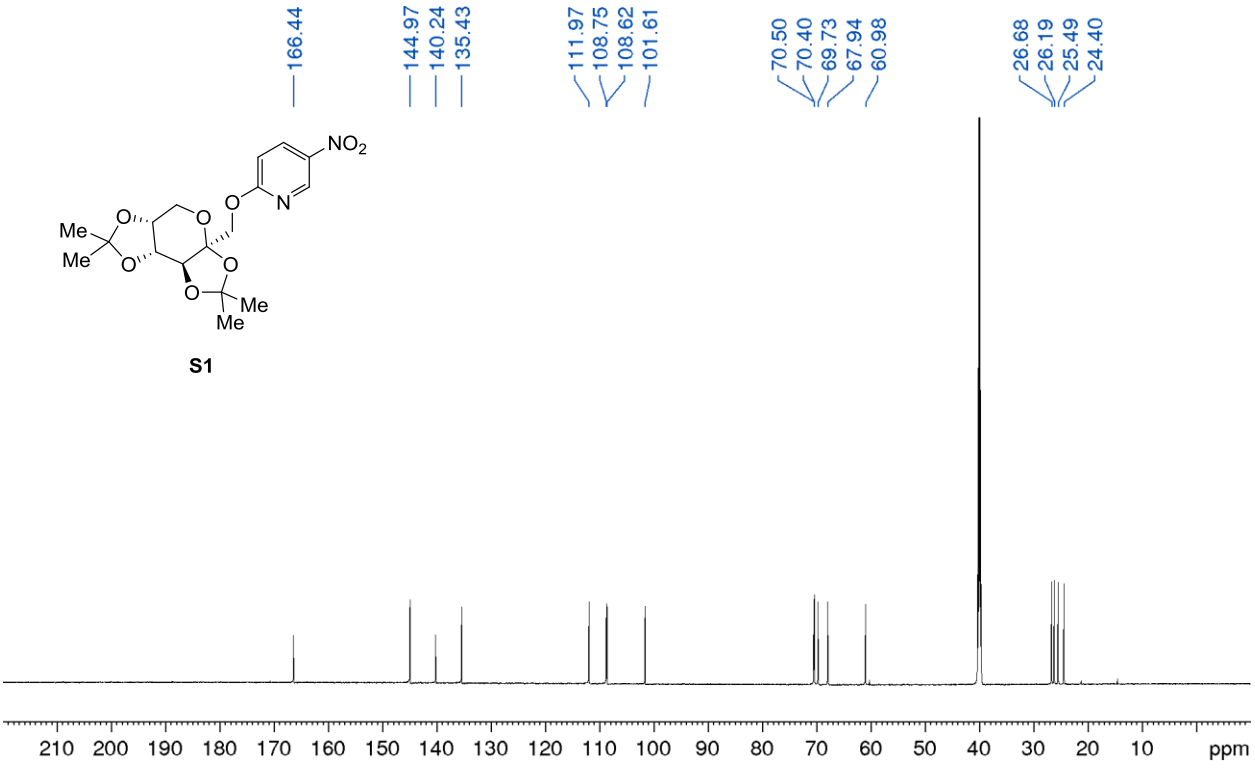
1. Still, W. C.; Kahn, M.; Mitra, A., *J. Org. Chem.* **1978,** *43* (14), 2923.
2. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010,** *29*, 2176.
3. Wang, X.; Xu, Y.; Mo, F.; Ji, G.; Qiu, D.; Feng, J.; Ye, Y.; Zhang, S.; Zhang, Y.; Wang, J., *J. Am. Chem. Soc.* **2013,** *135*, 10330.

Spectroscopic Data

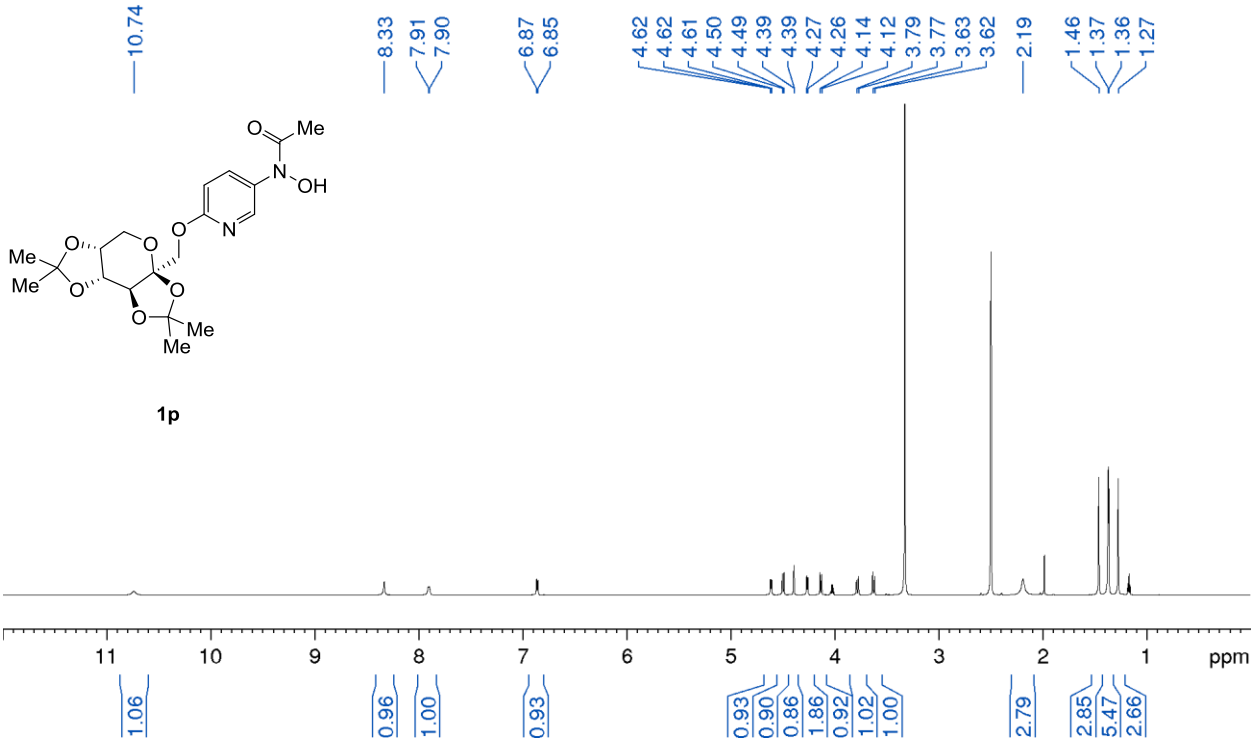
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (S1)



^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (S1)

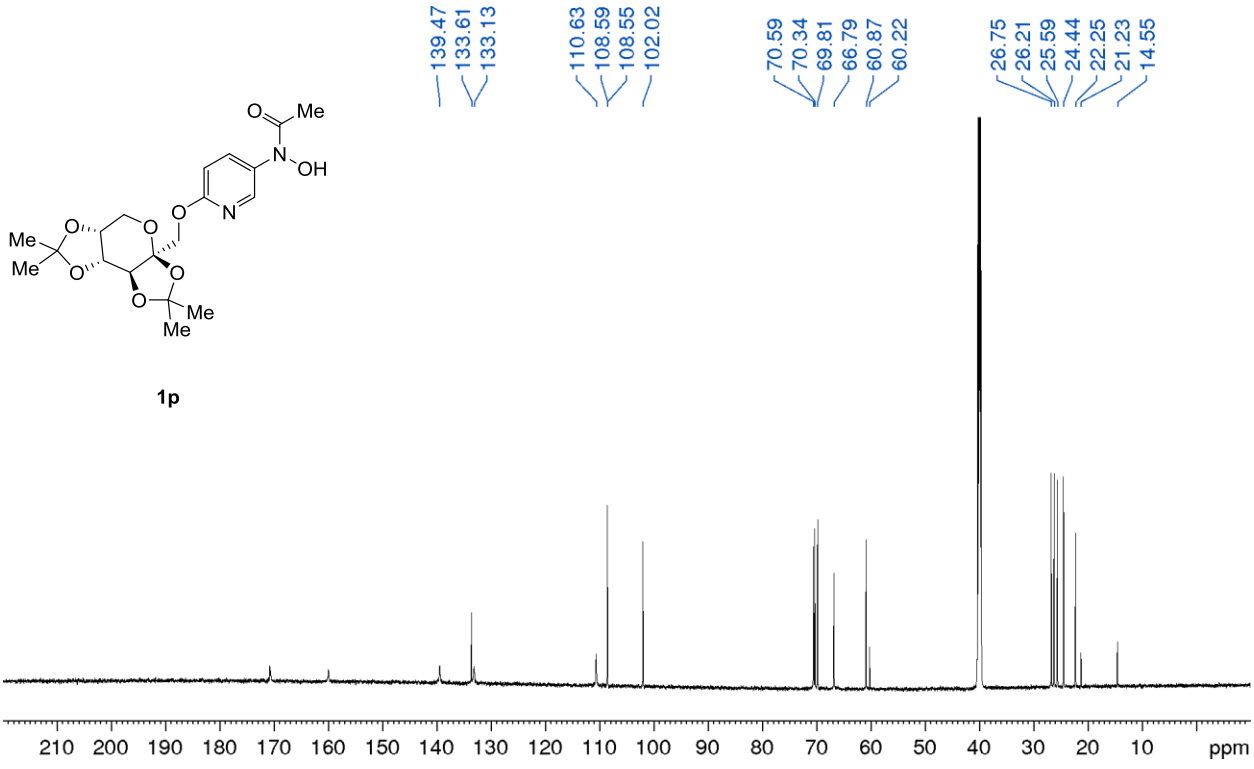


^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (1p)



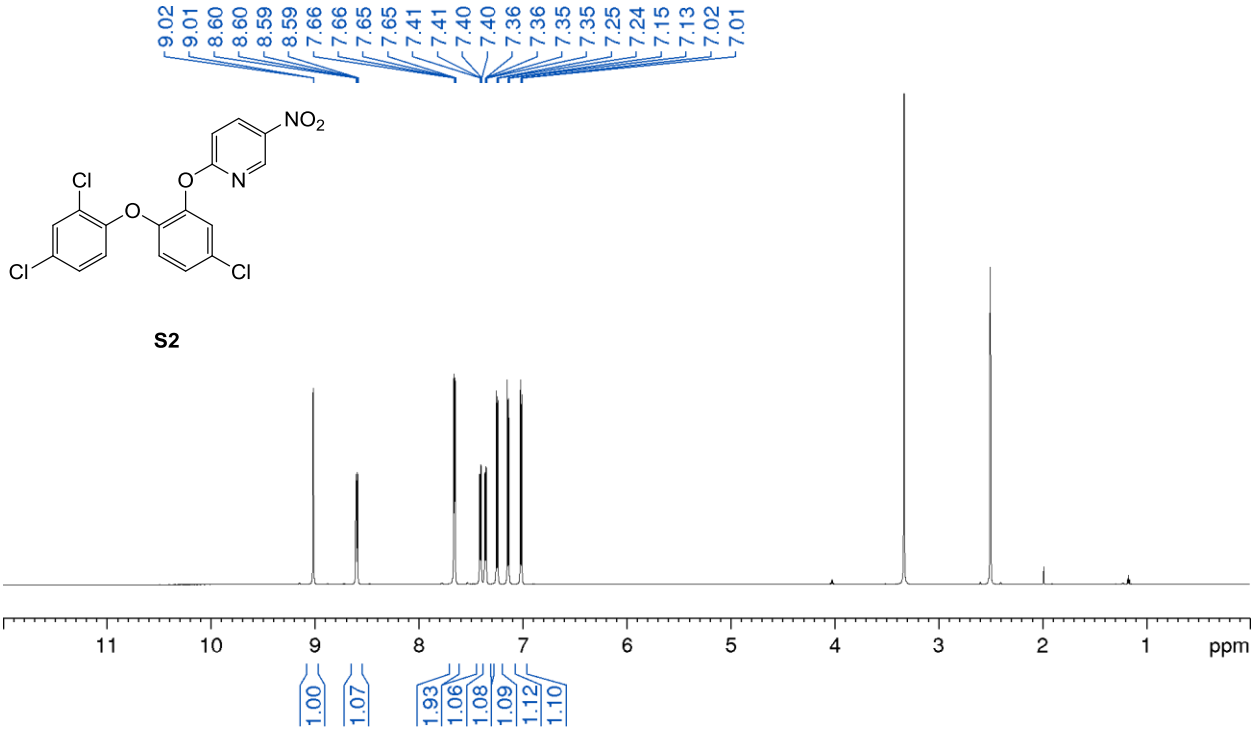
1p

^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (1p)

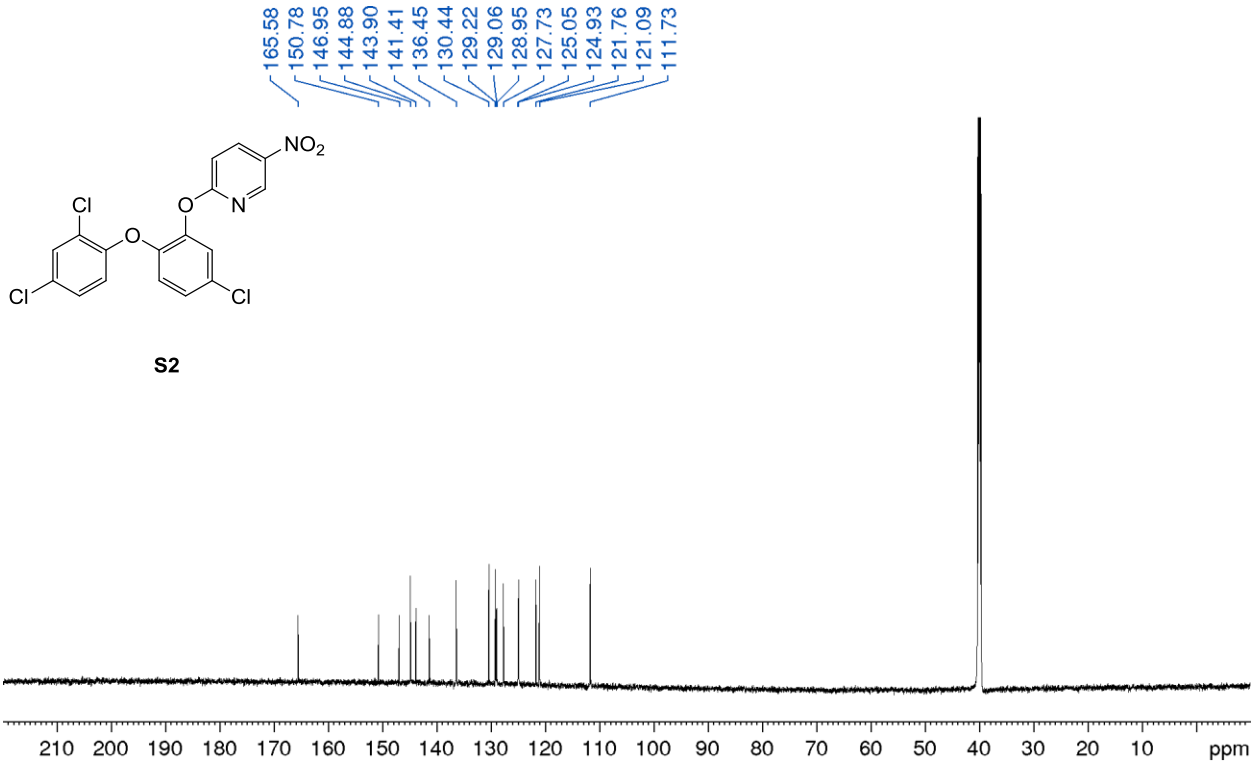


1p

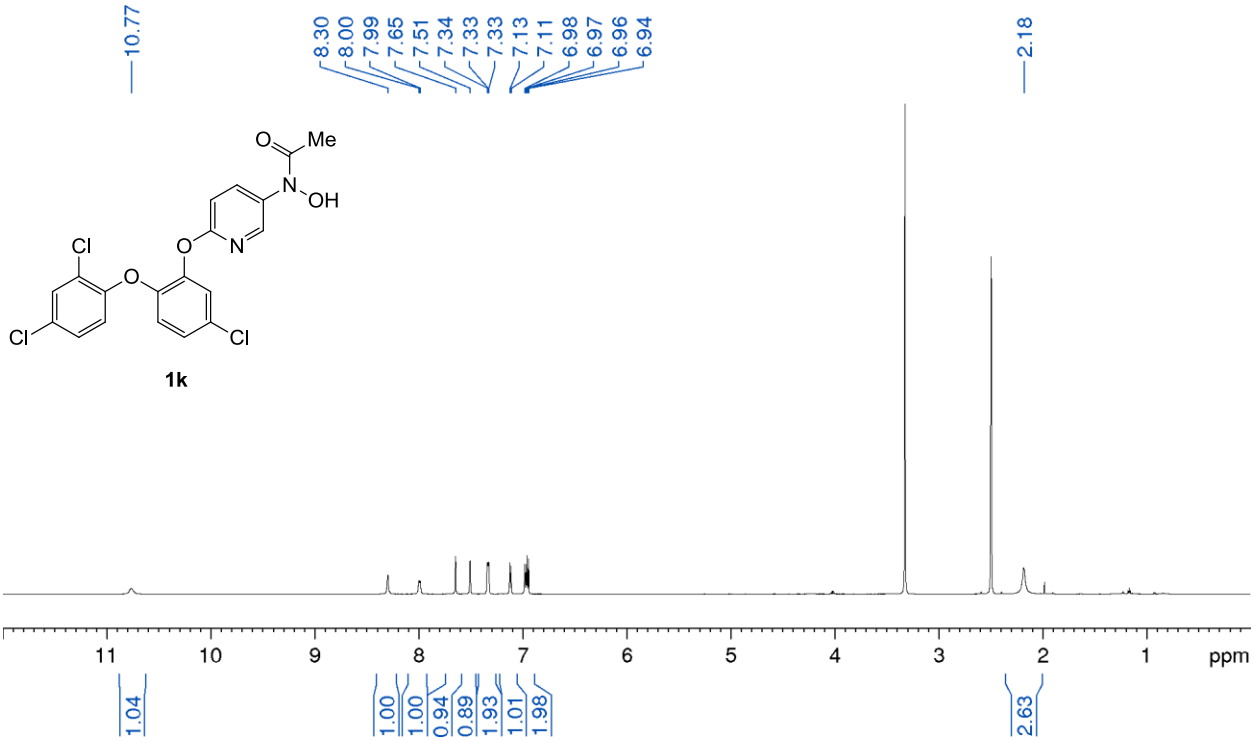
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (S2)



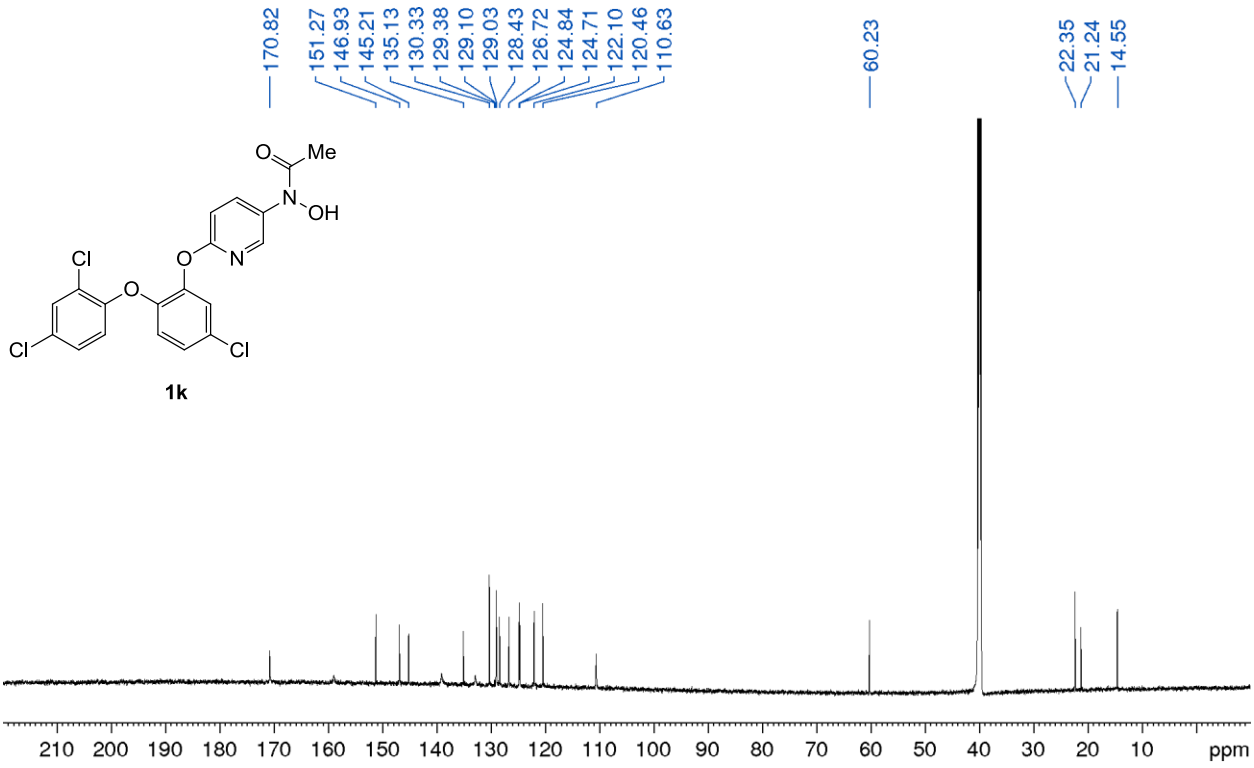
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (S2)



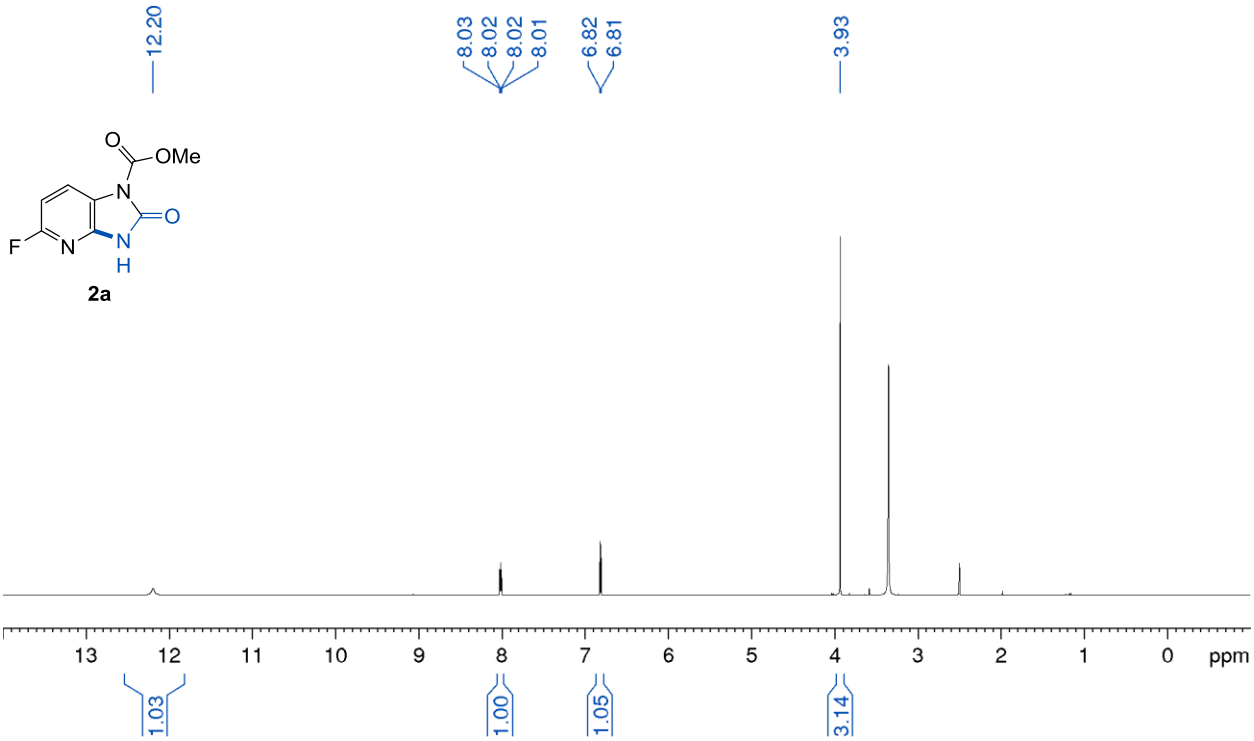
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (1k)



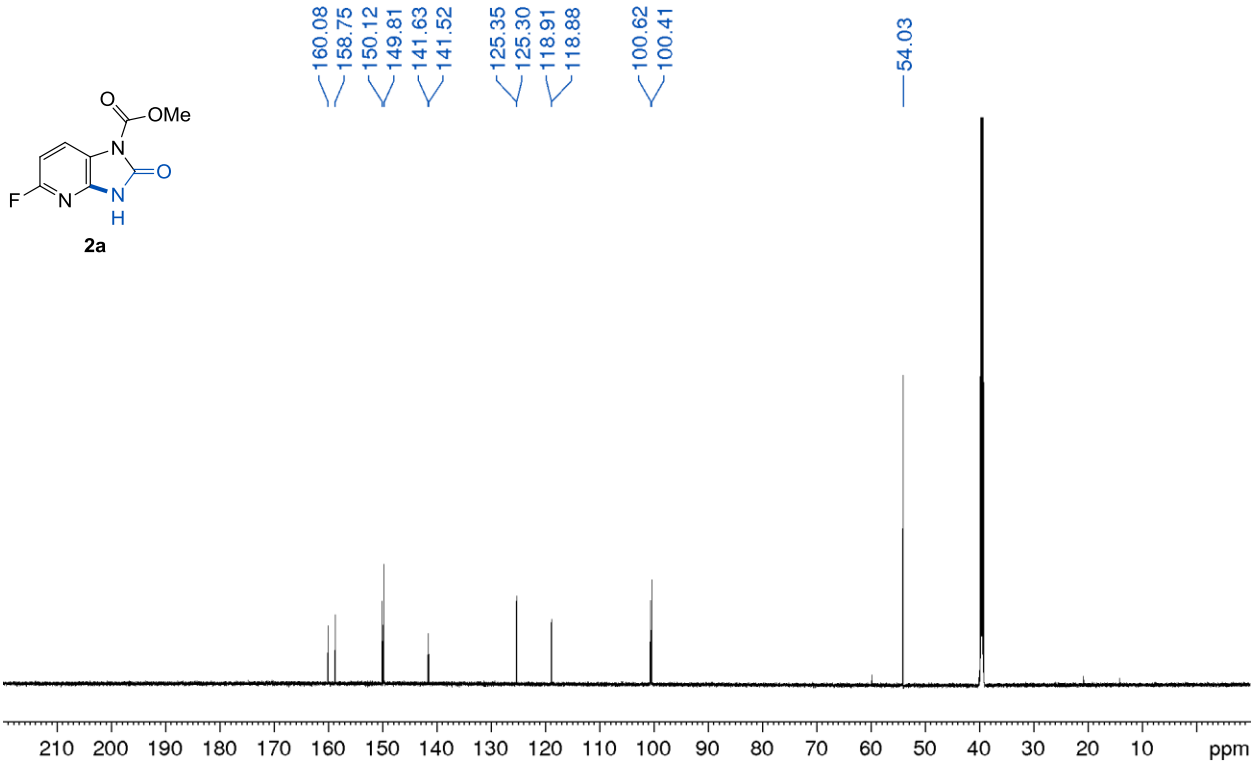
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (1k)



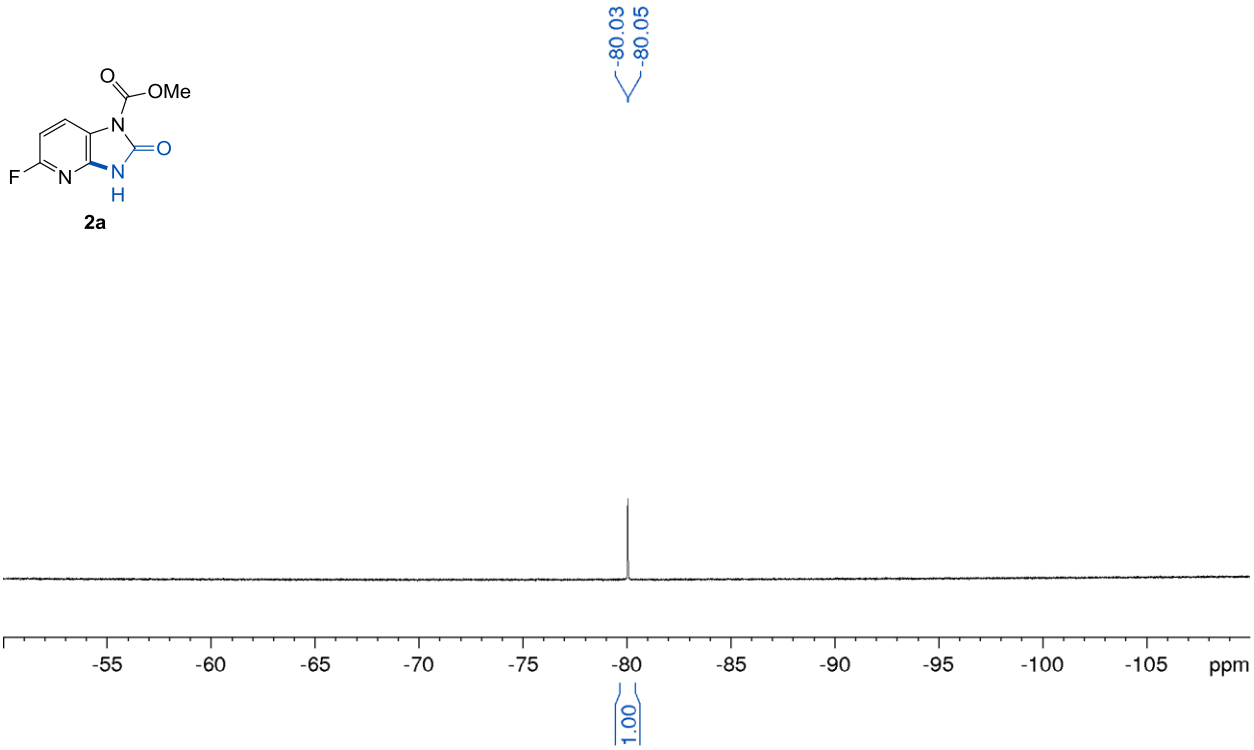
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2a)



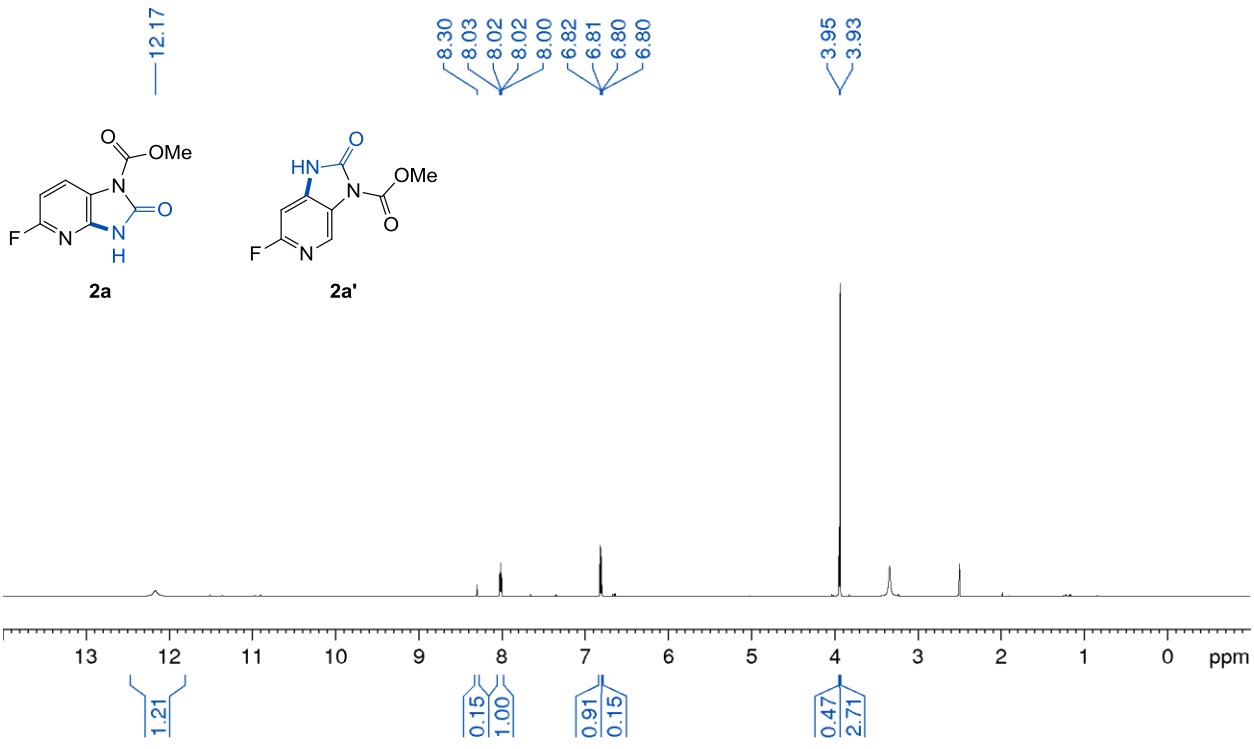
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2a)



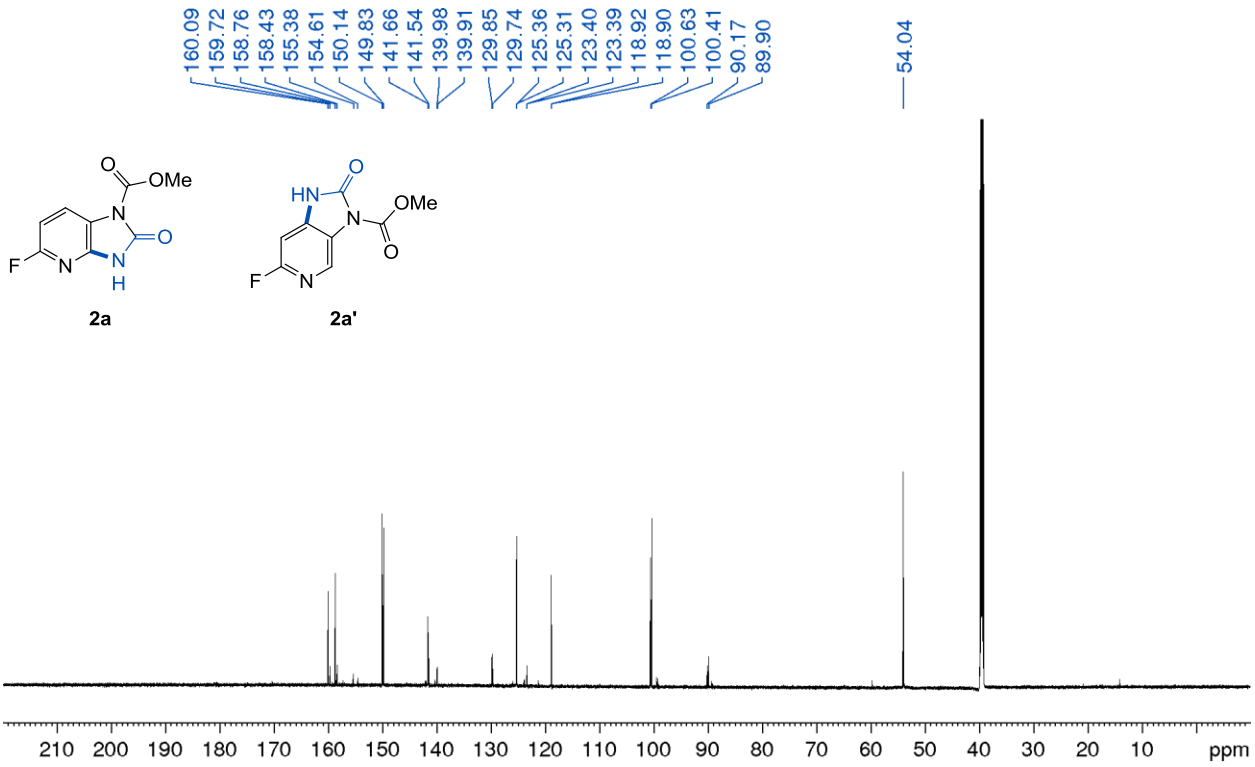
^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC) of (2a)



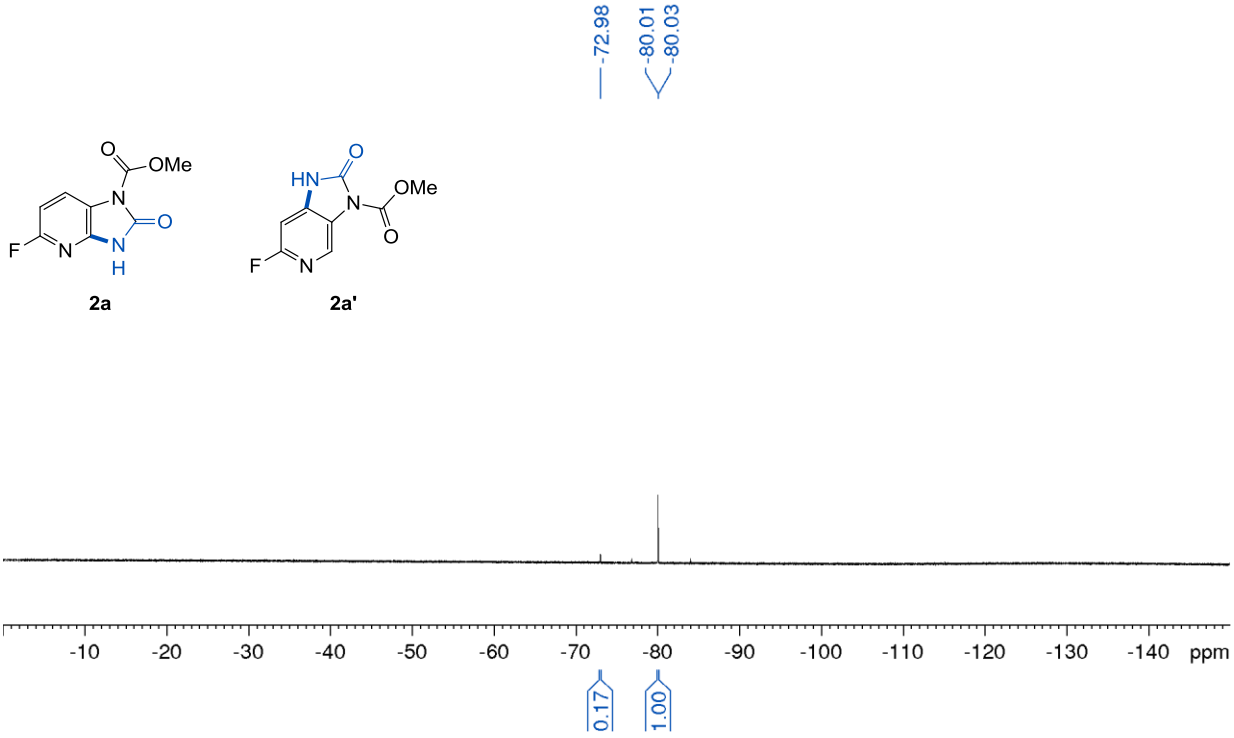
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (2a and 2a')



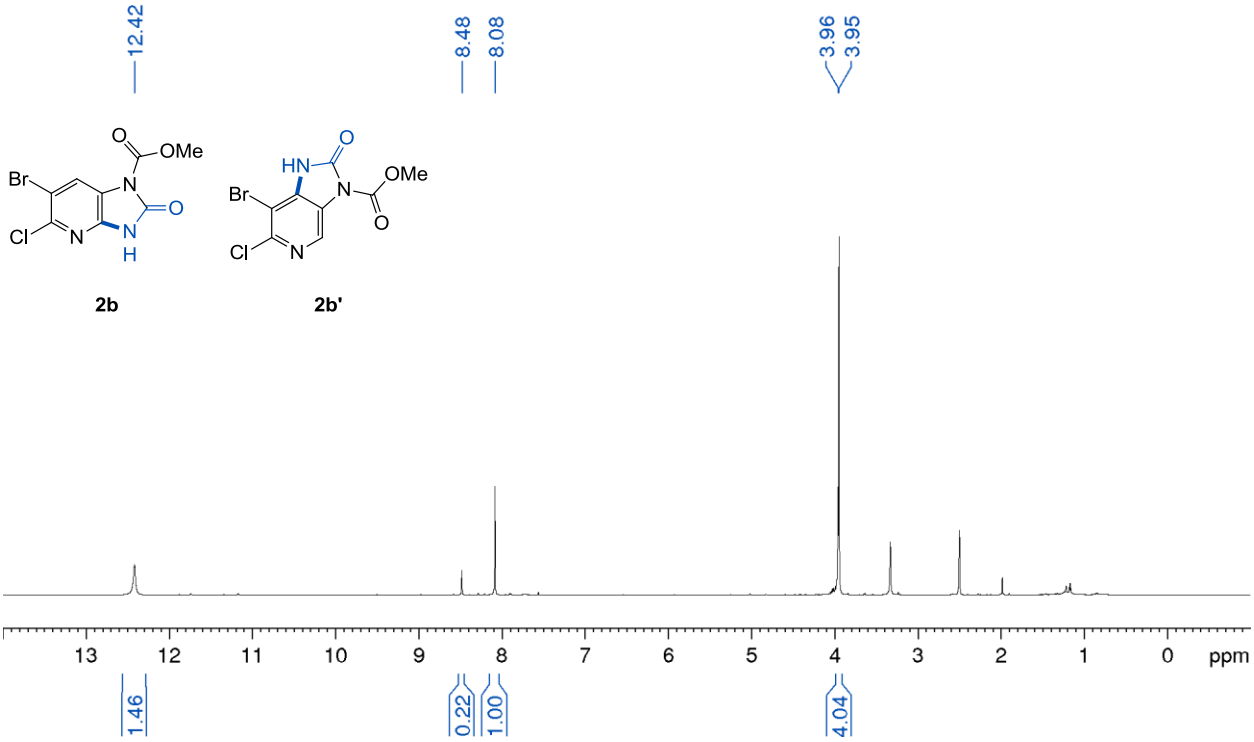
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (2a and 2a')



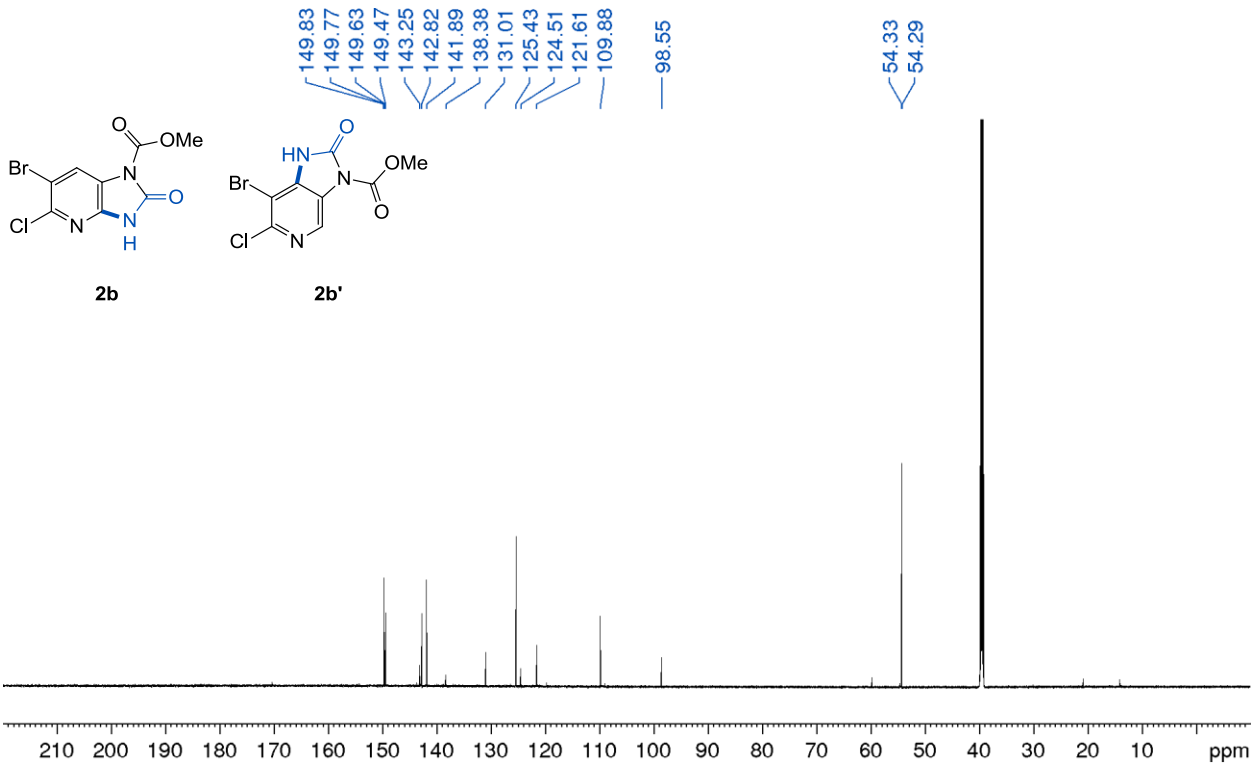
^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC) of (2a and 2a')



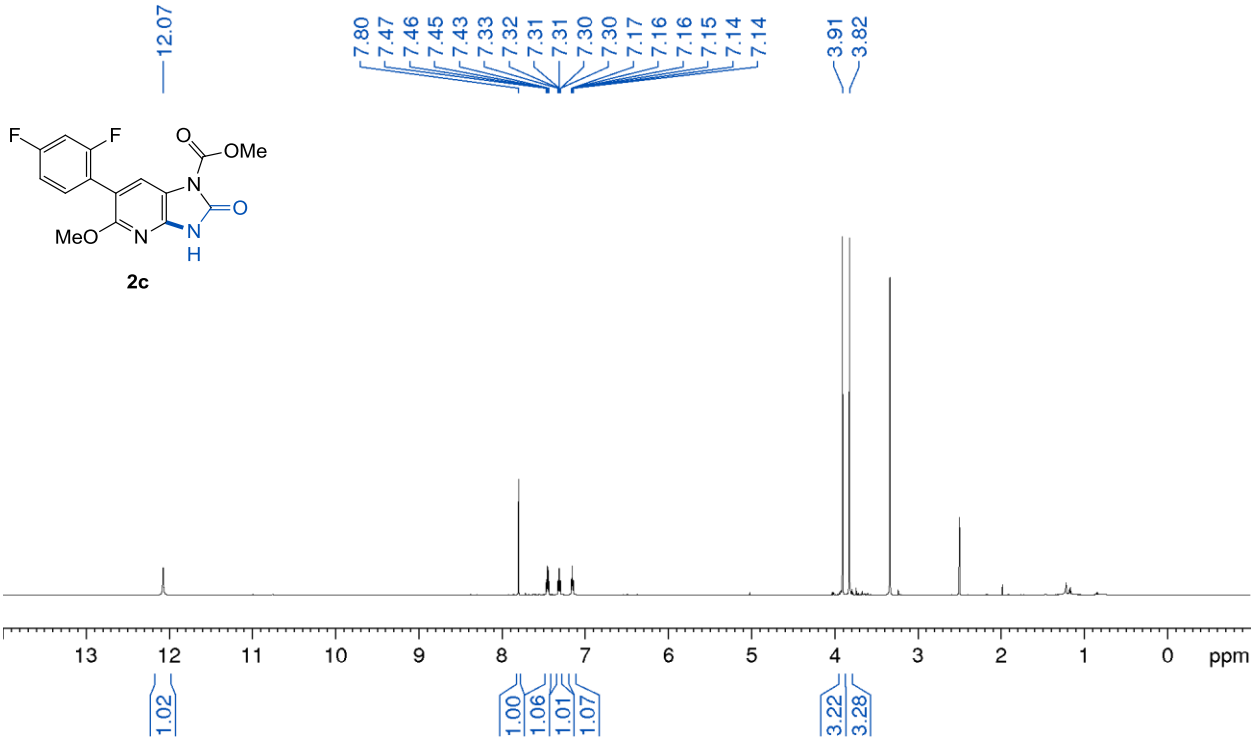
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2b and 2b')



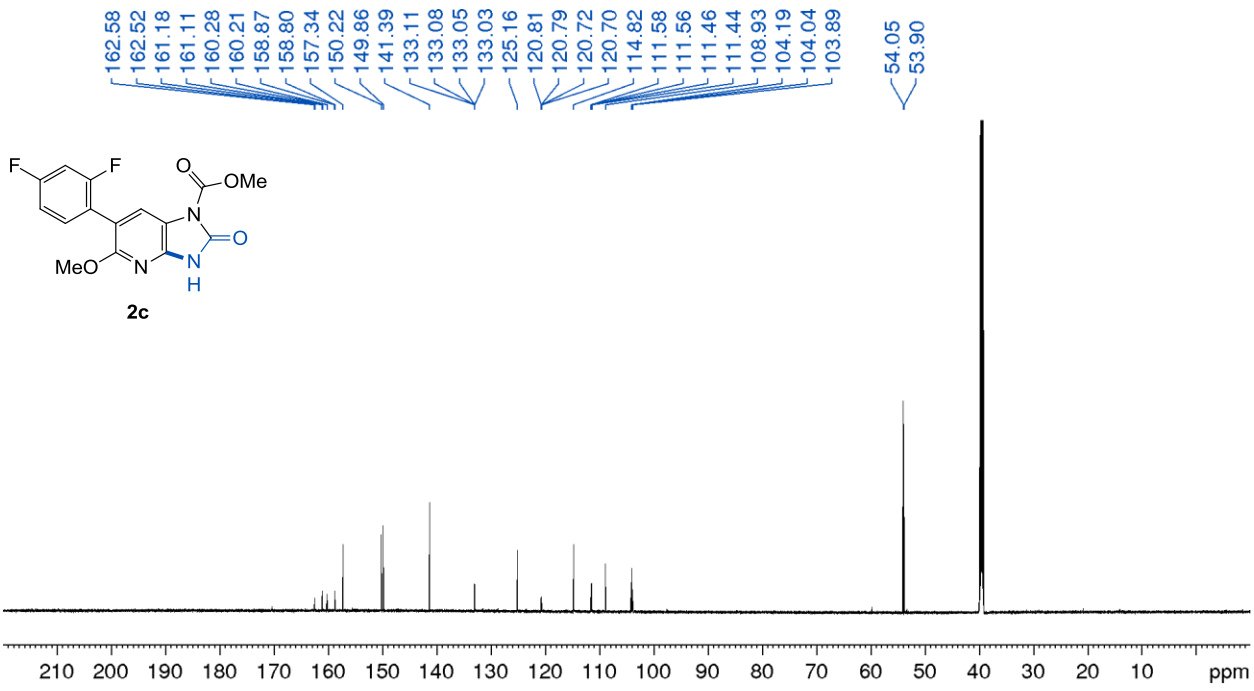
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2b and 2b')



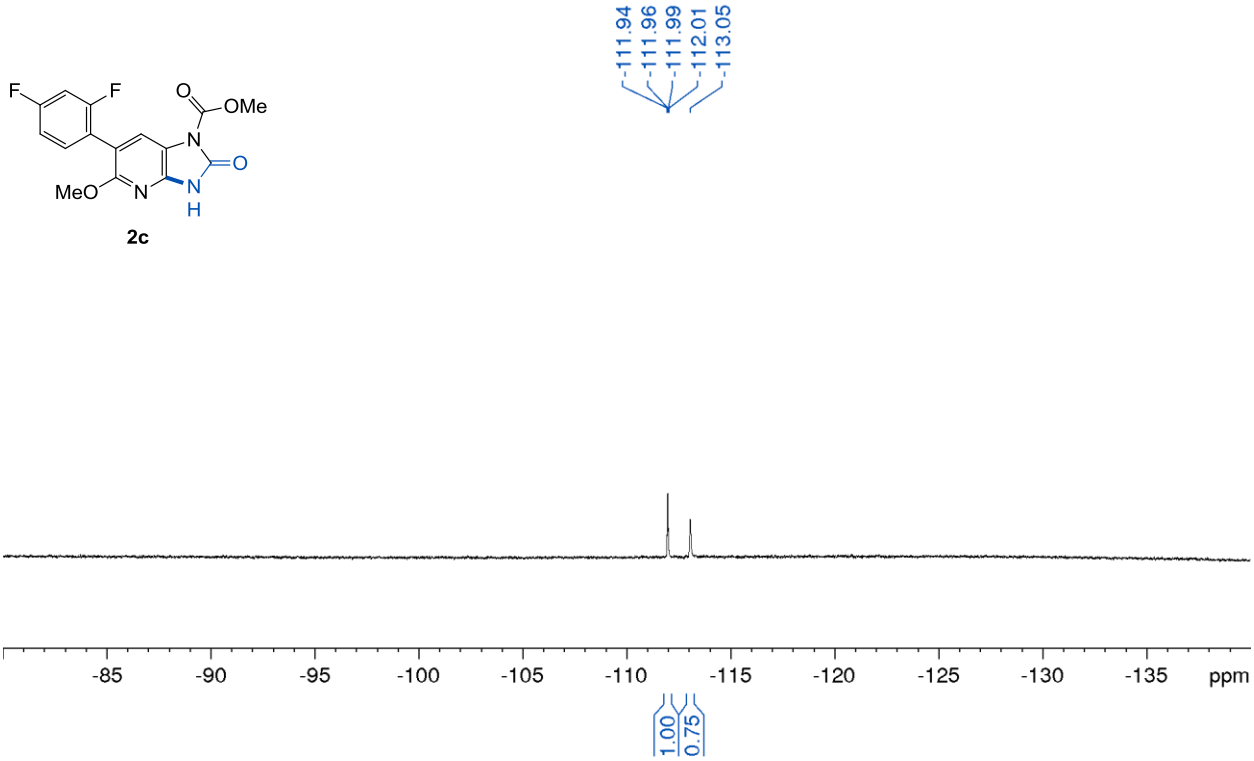
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2c)



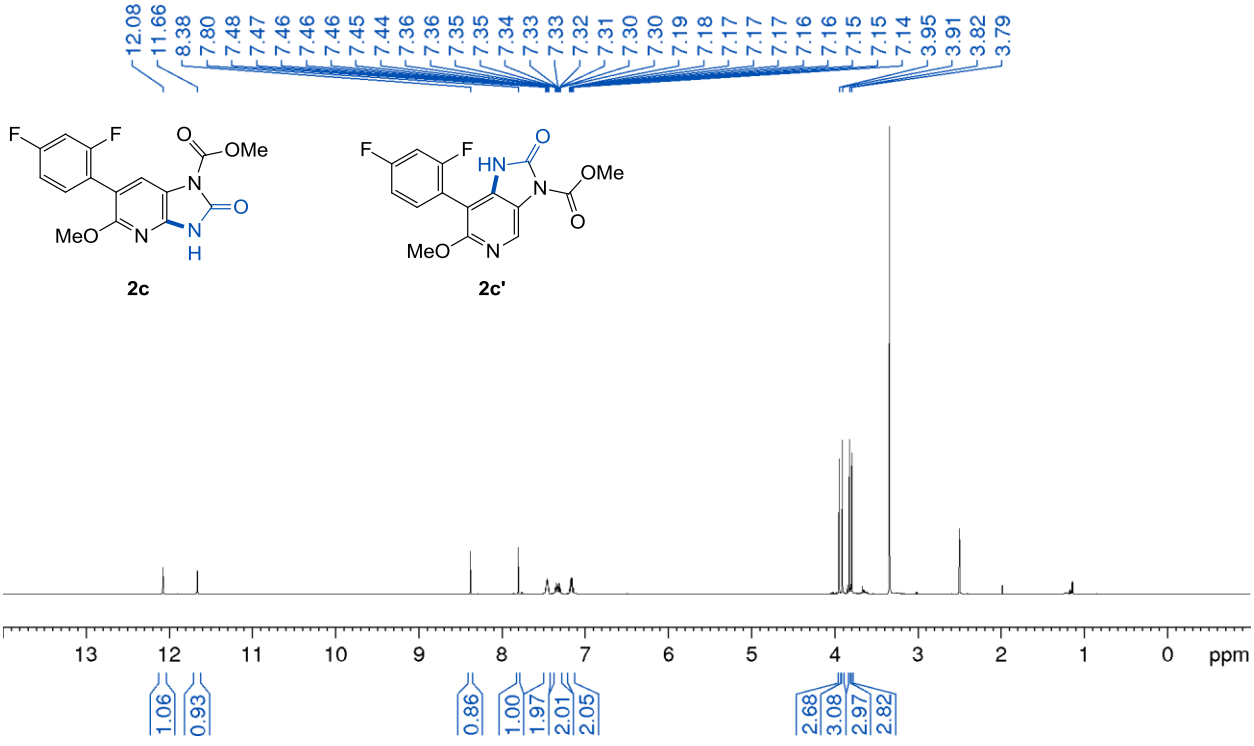
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2c)



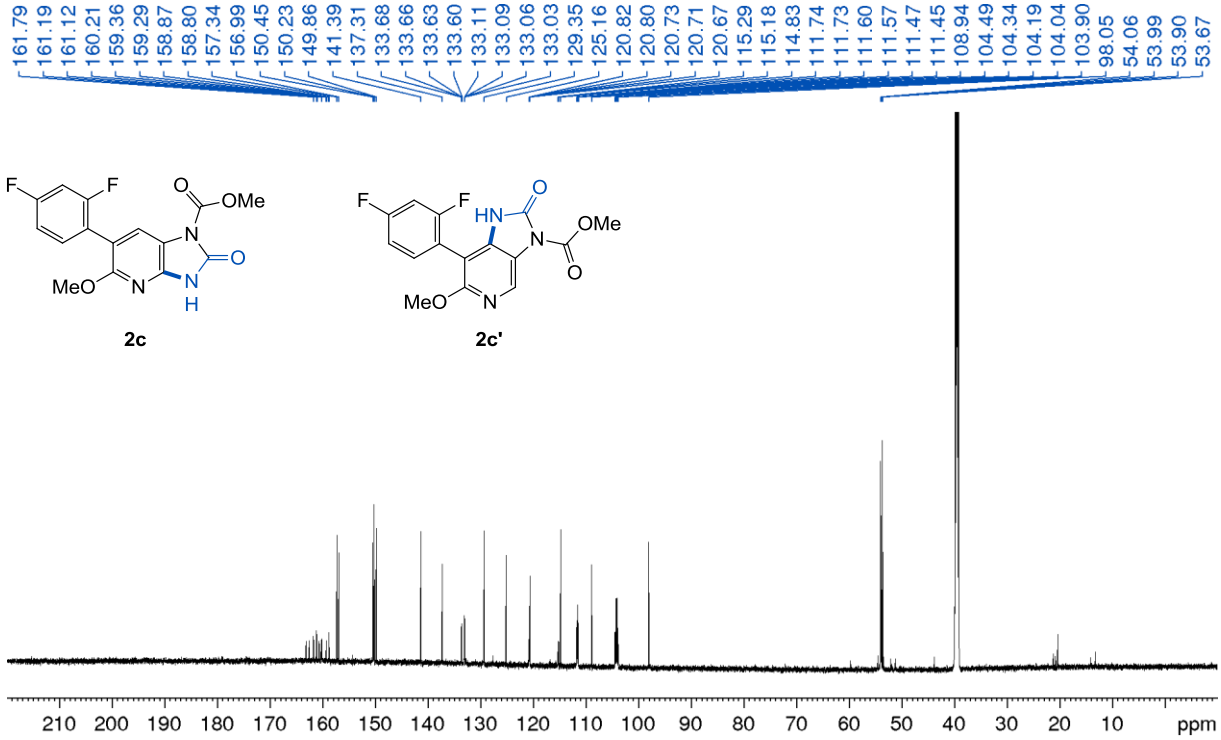
^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC) of (2c)



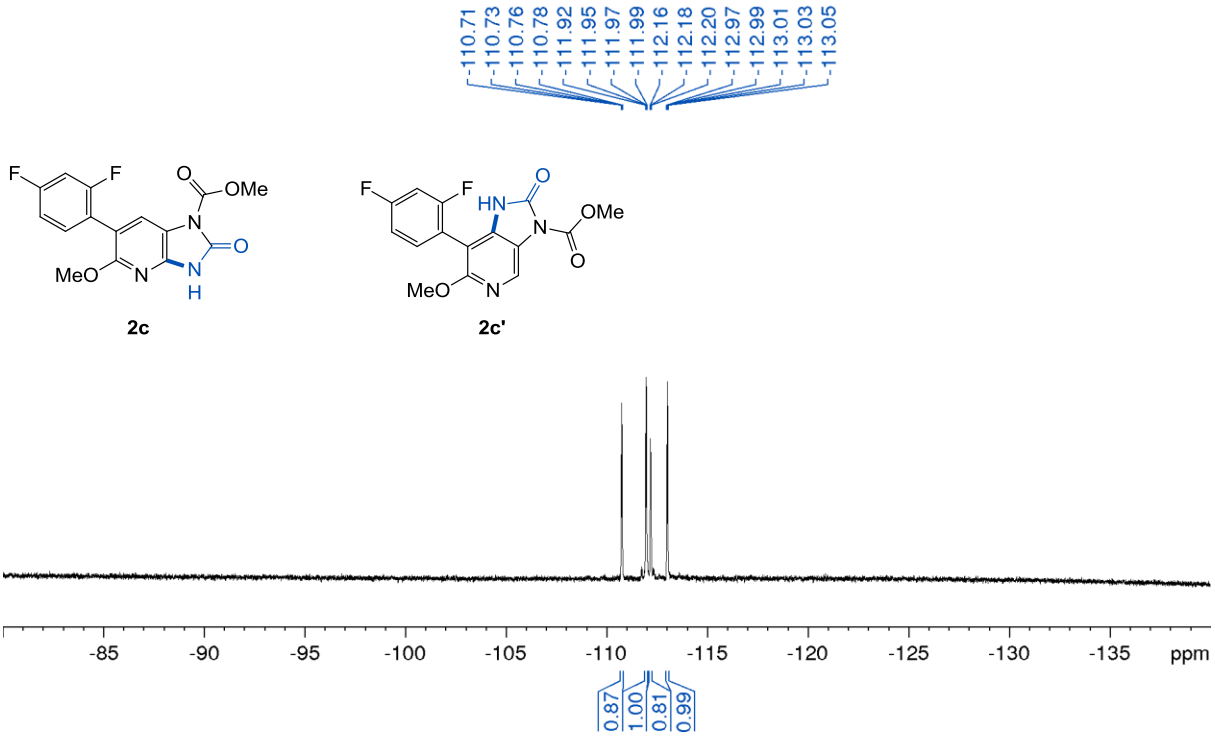
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (2c and 2c')



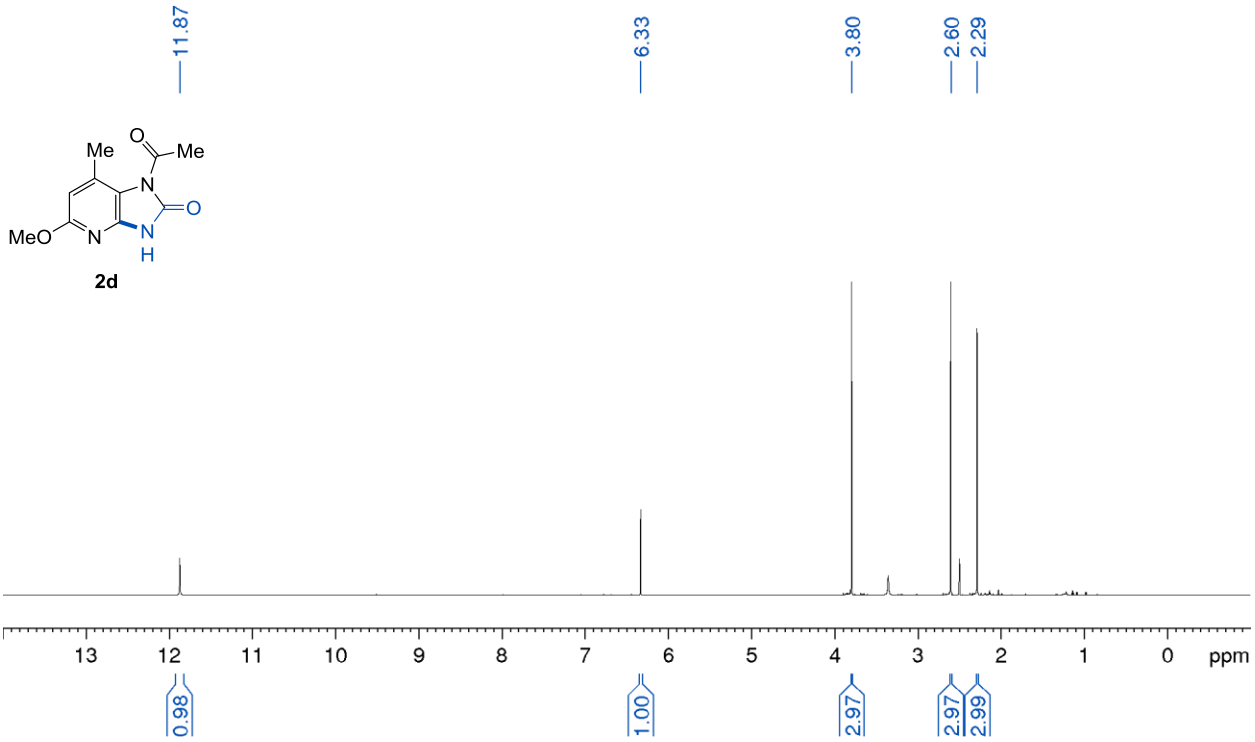
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (2c and 2c')



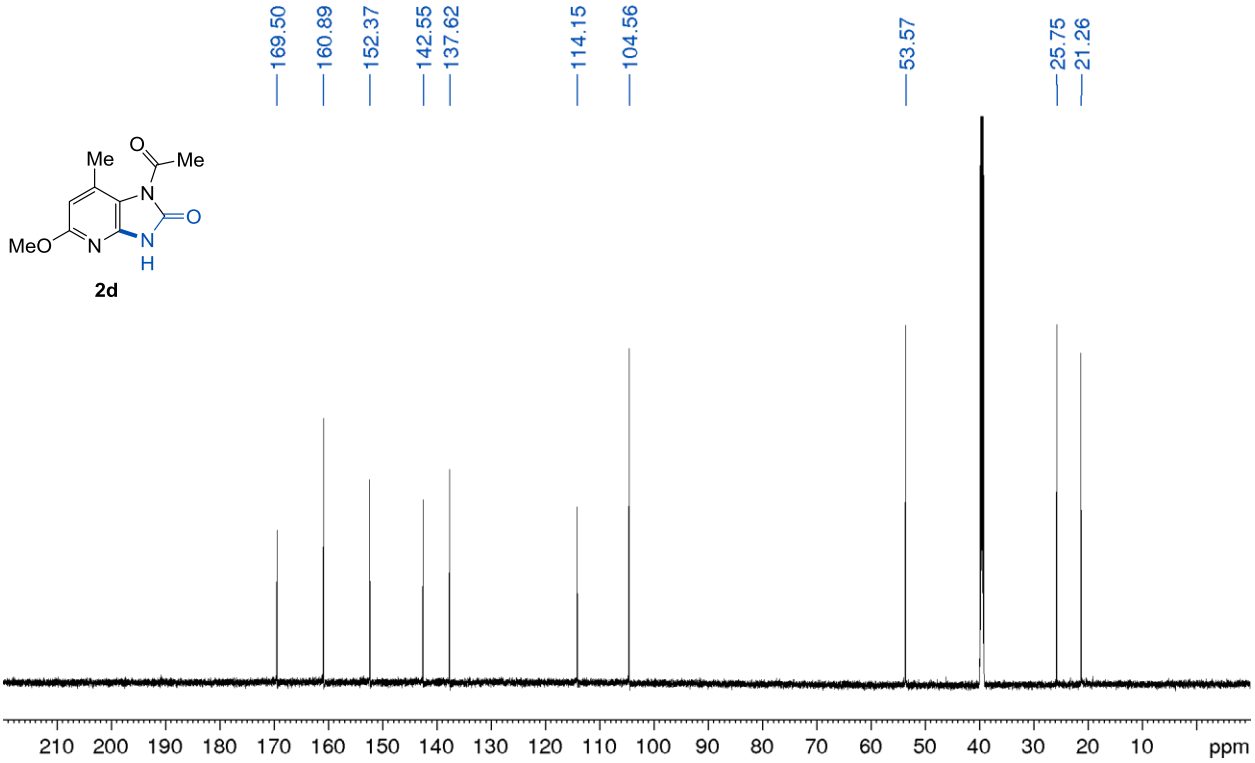
^{19}F NMR (376 MHz, $(CD_3)_2SO$, 25 ºC) of (2c and 2c')



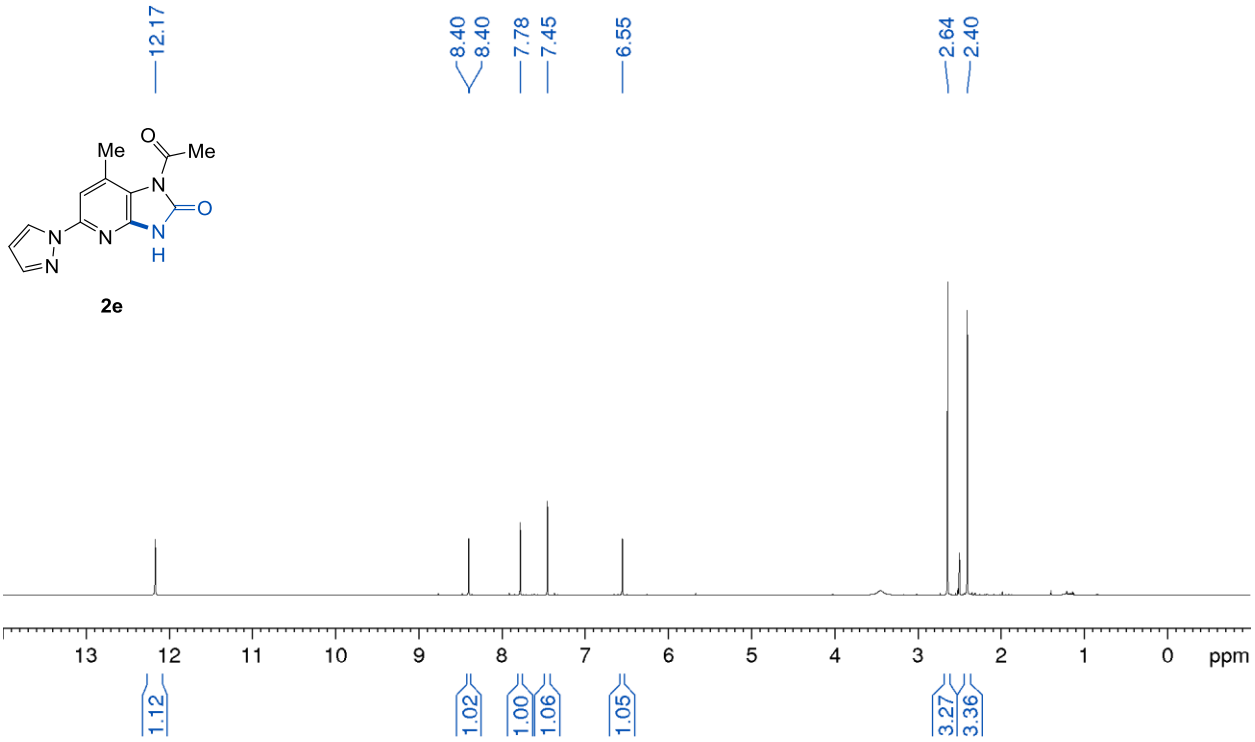
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2d)



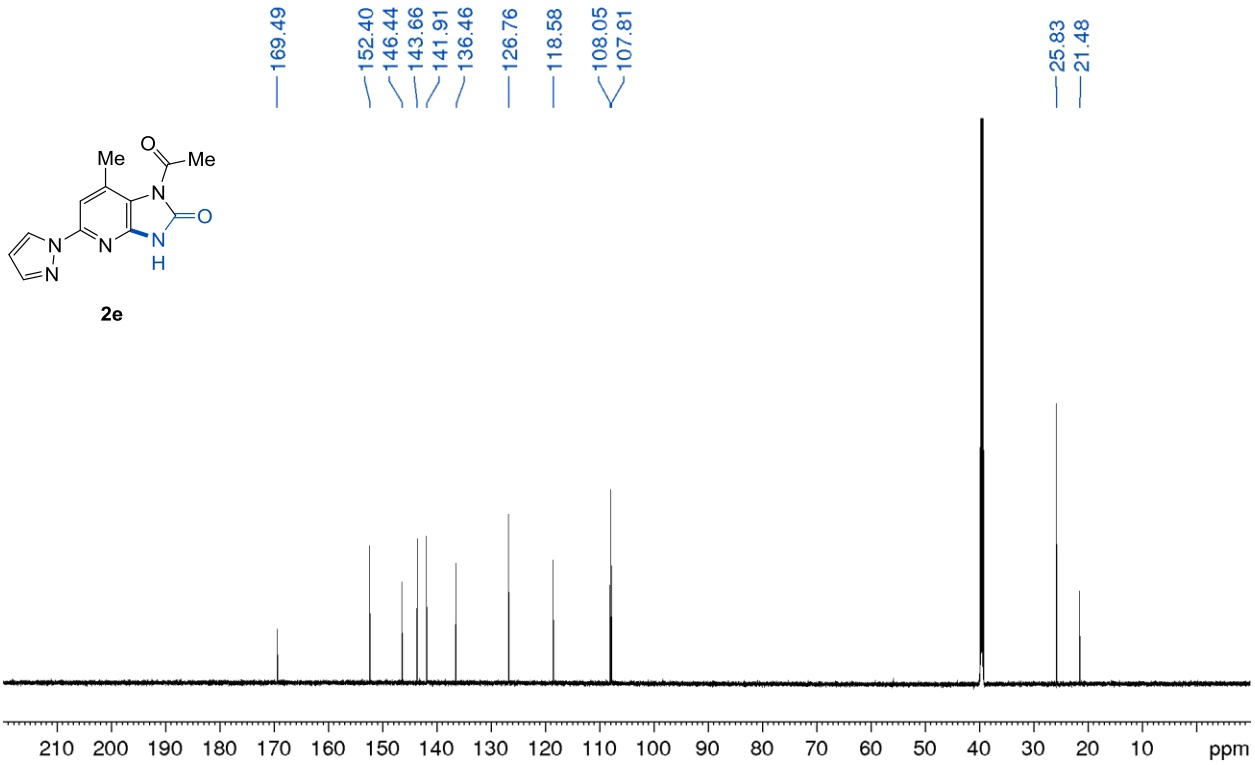
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2d)



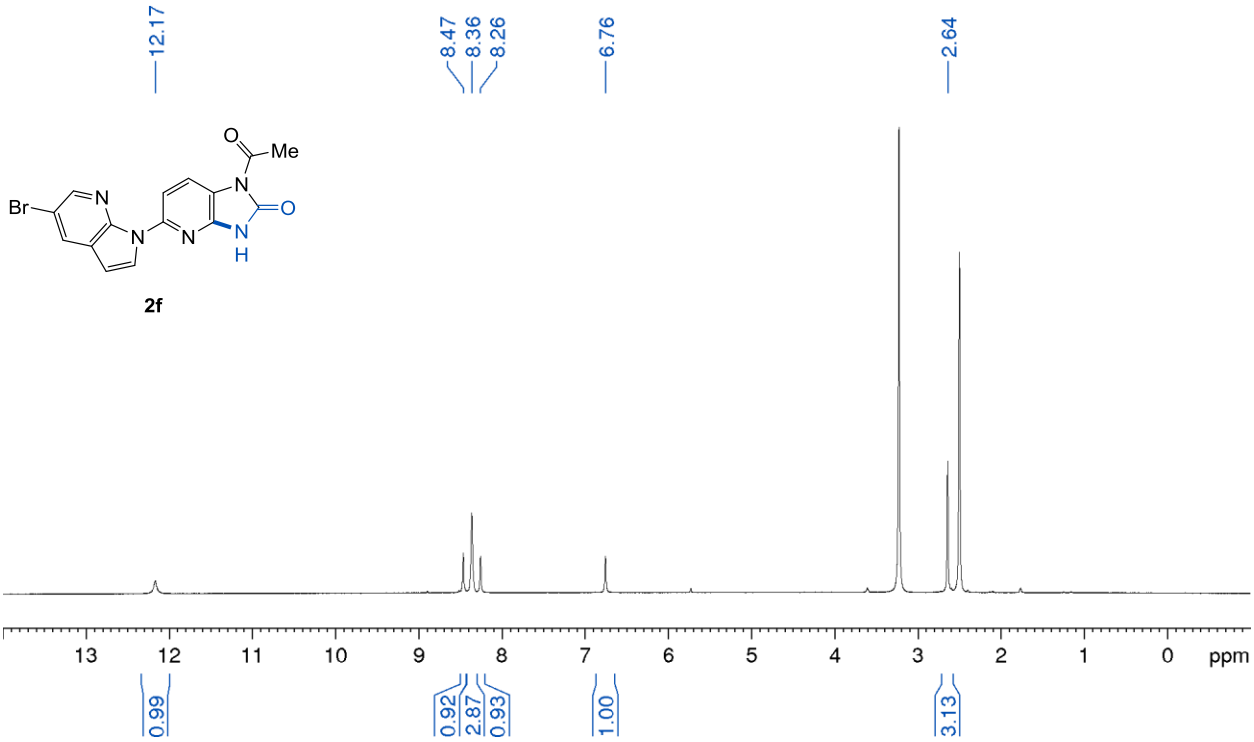
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2e)



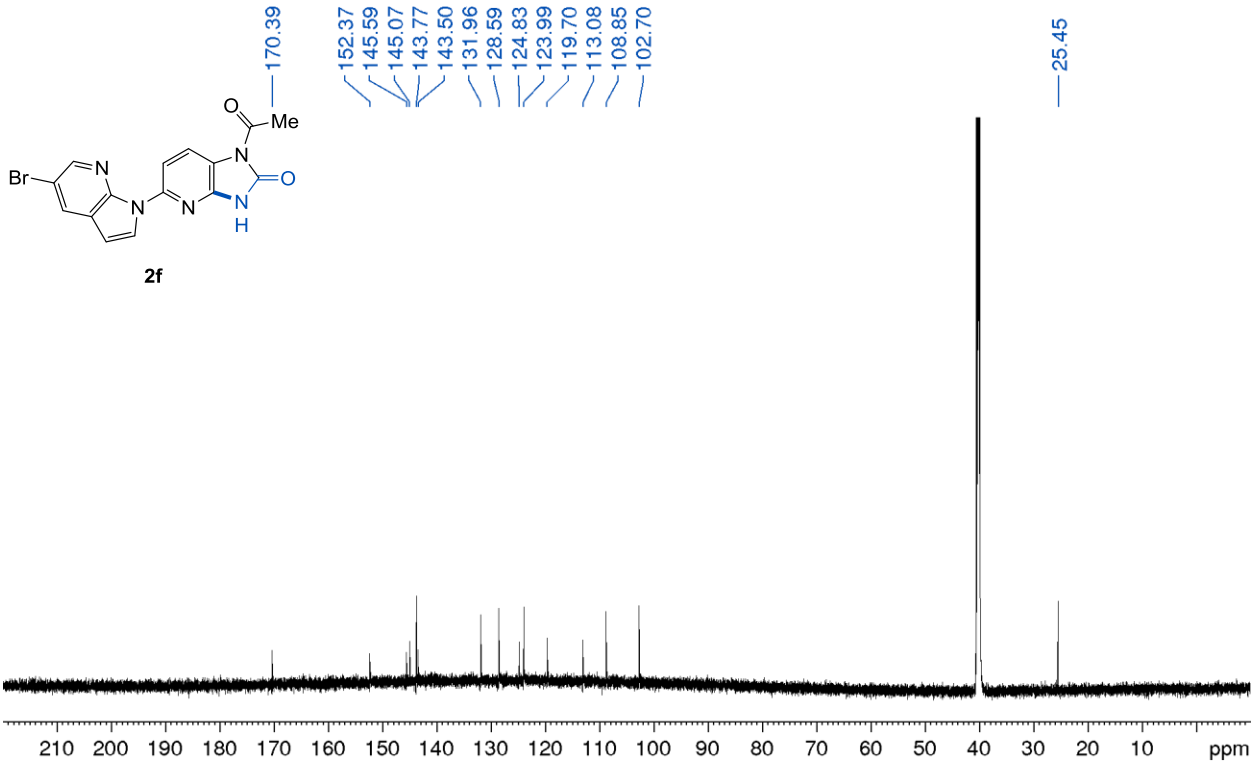
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2e)



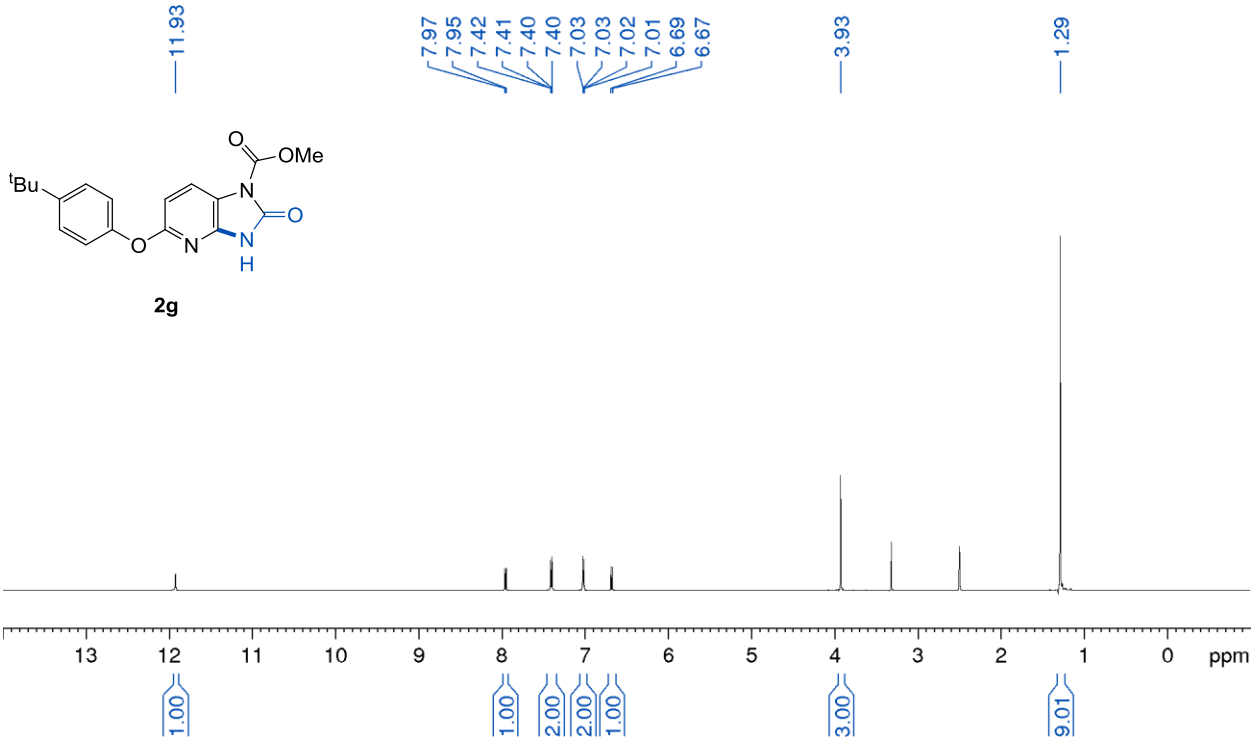
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2f)



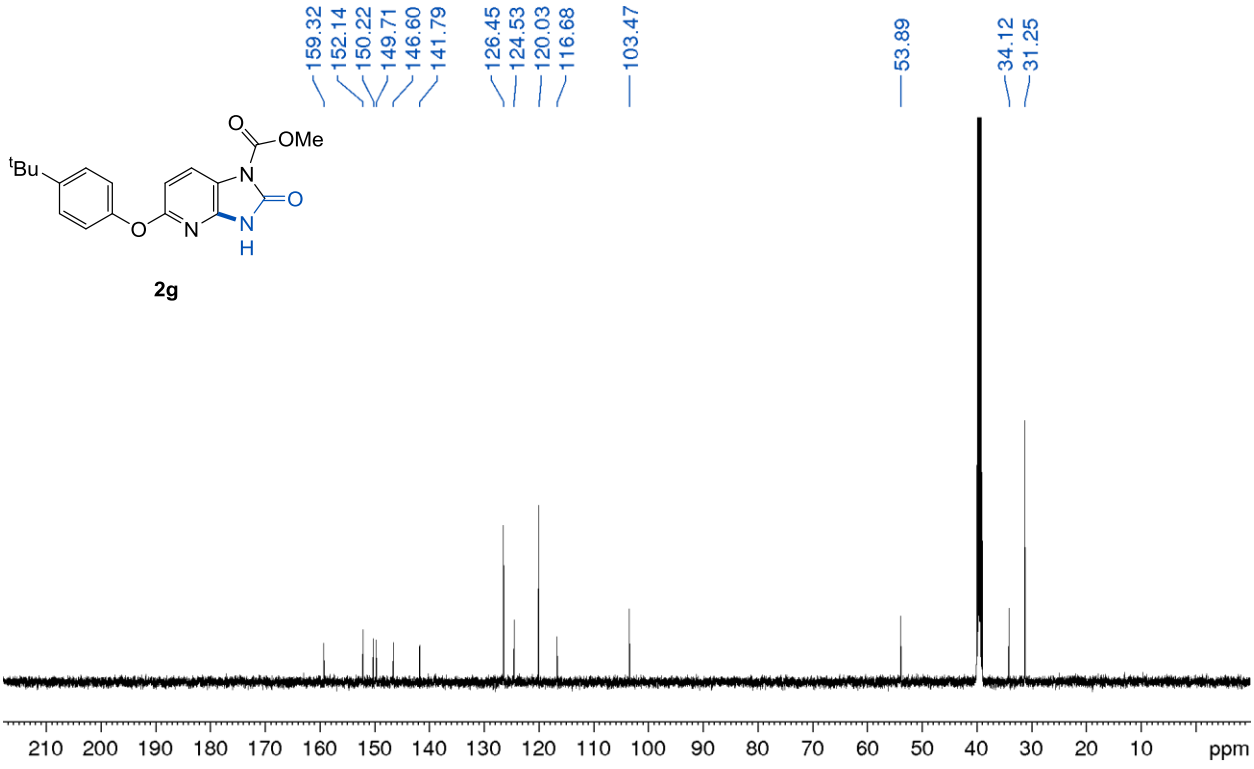
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2f)



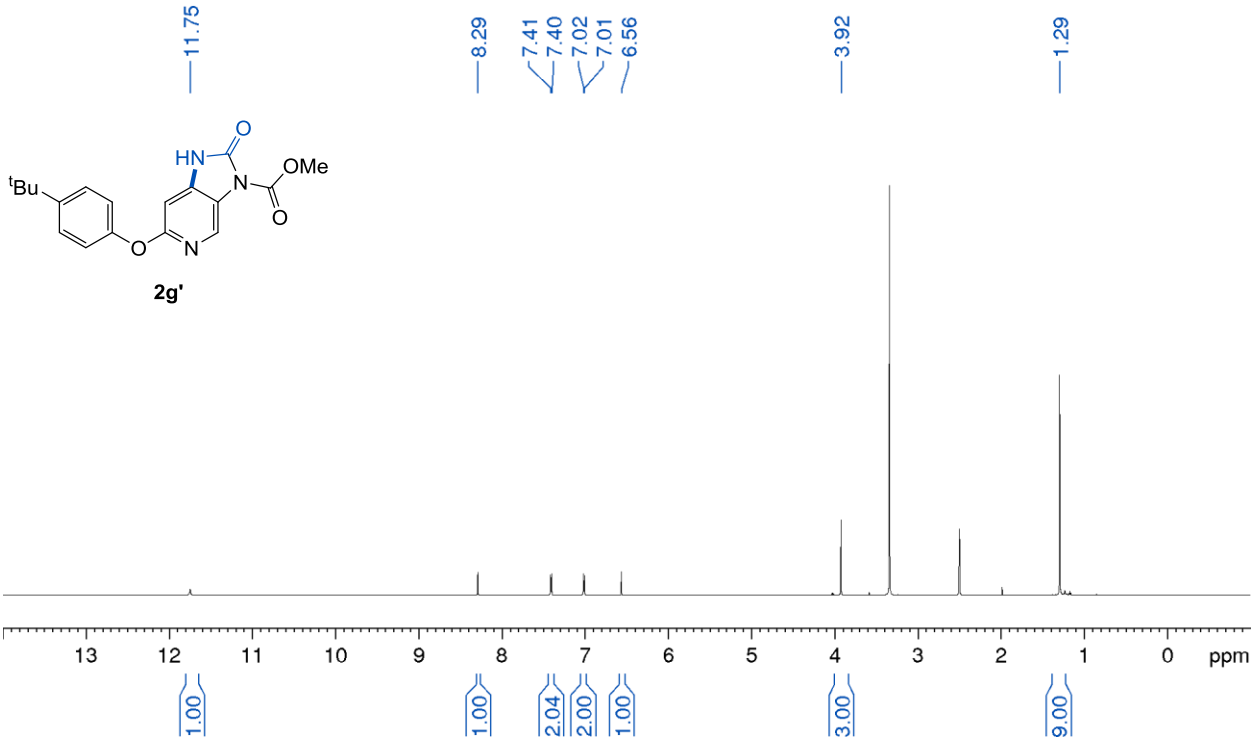
^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C) of (2g)



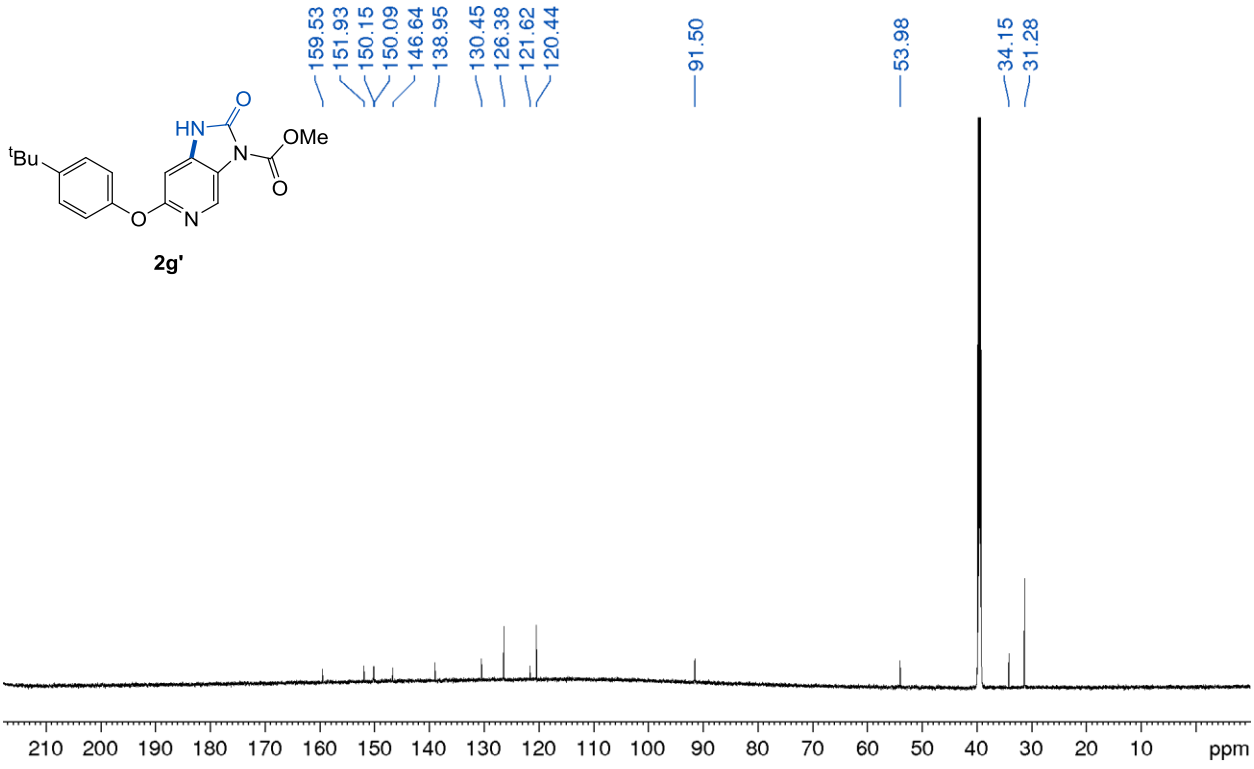
^{13}C NMR (125 MHz, $(CD_3)_2SO$, 25 °C) of (2g)



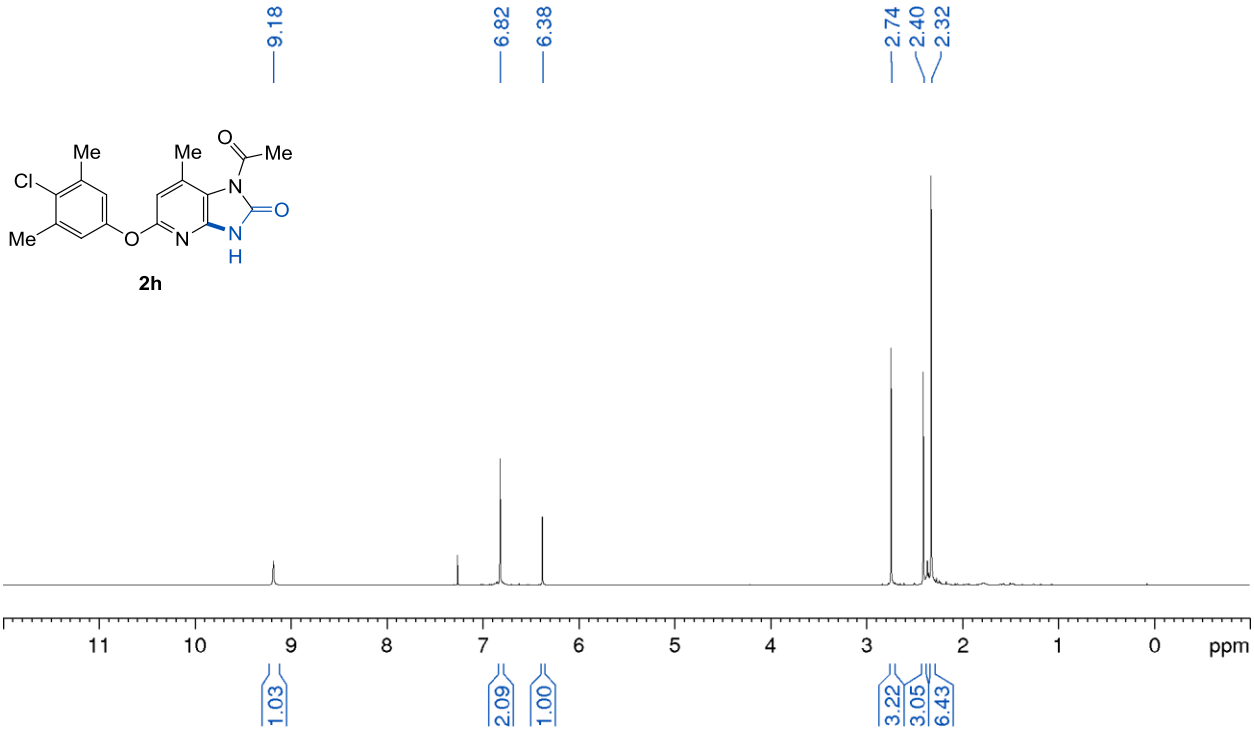
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (2g')



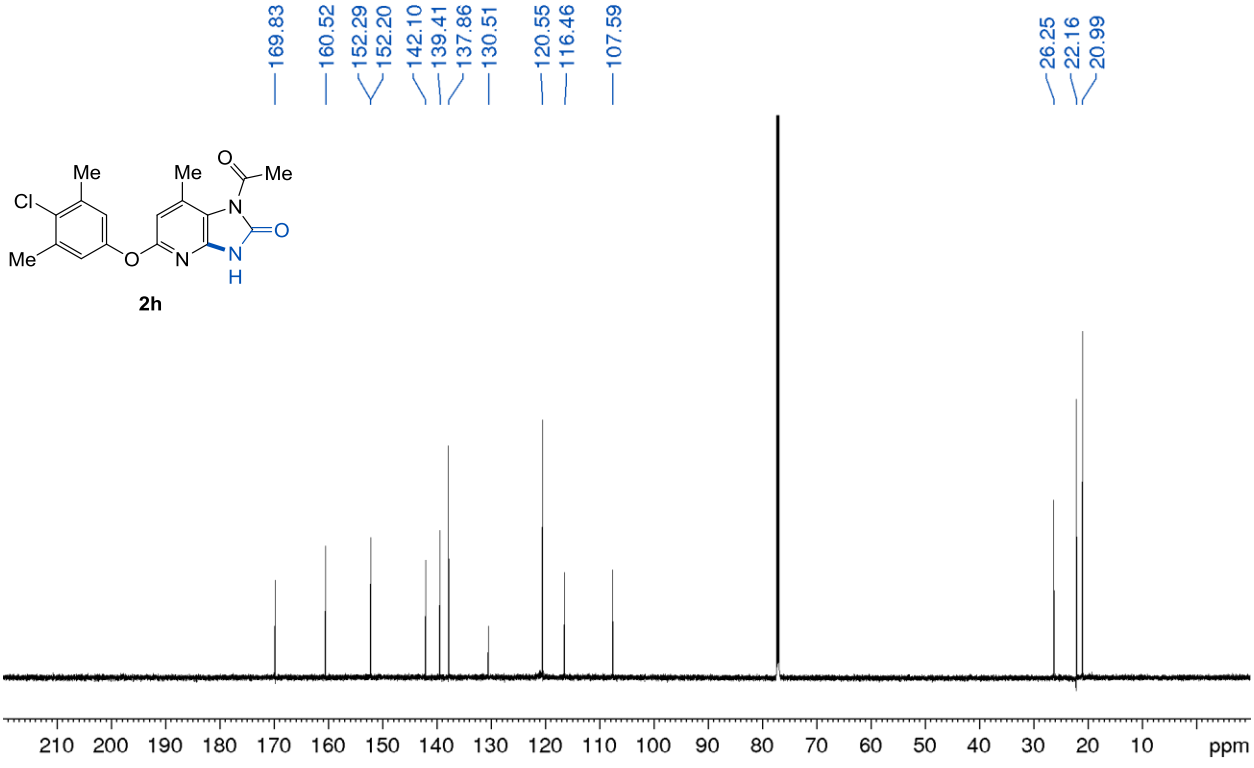
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (2g')



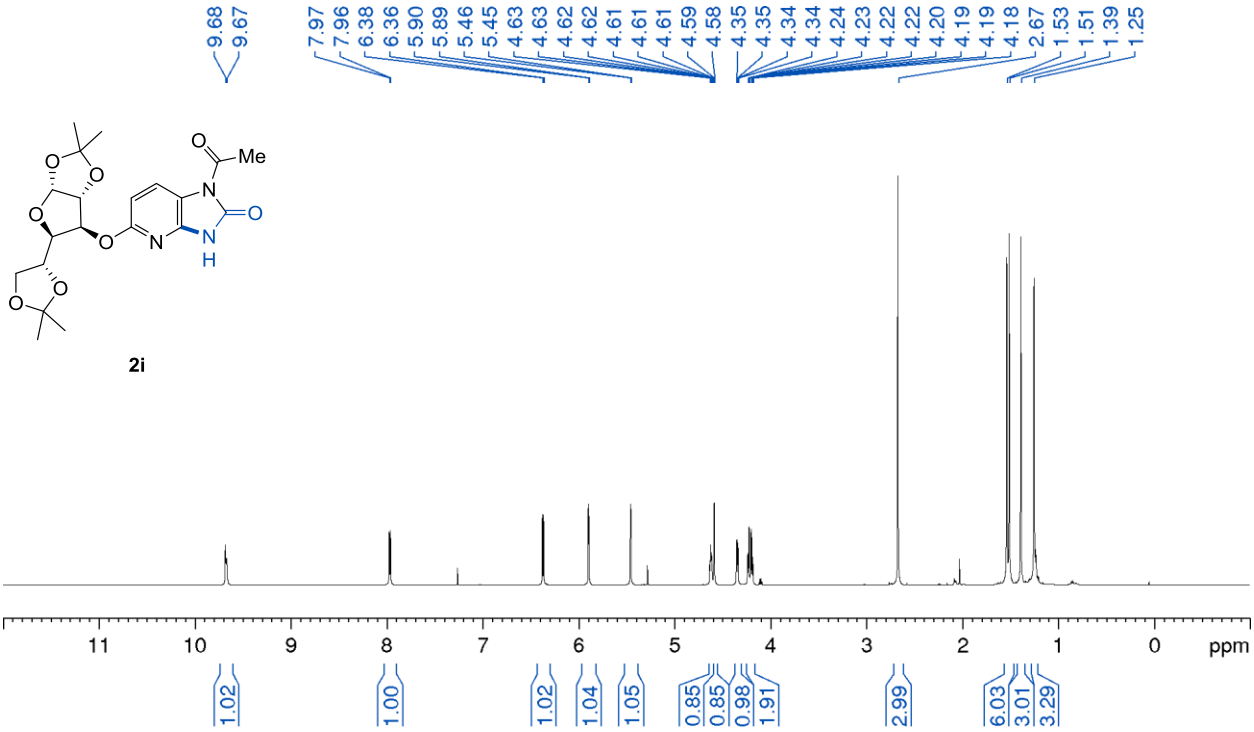
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2h)



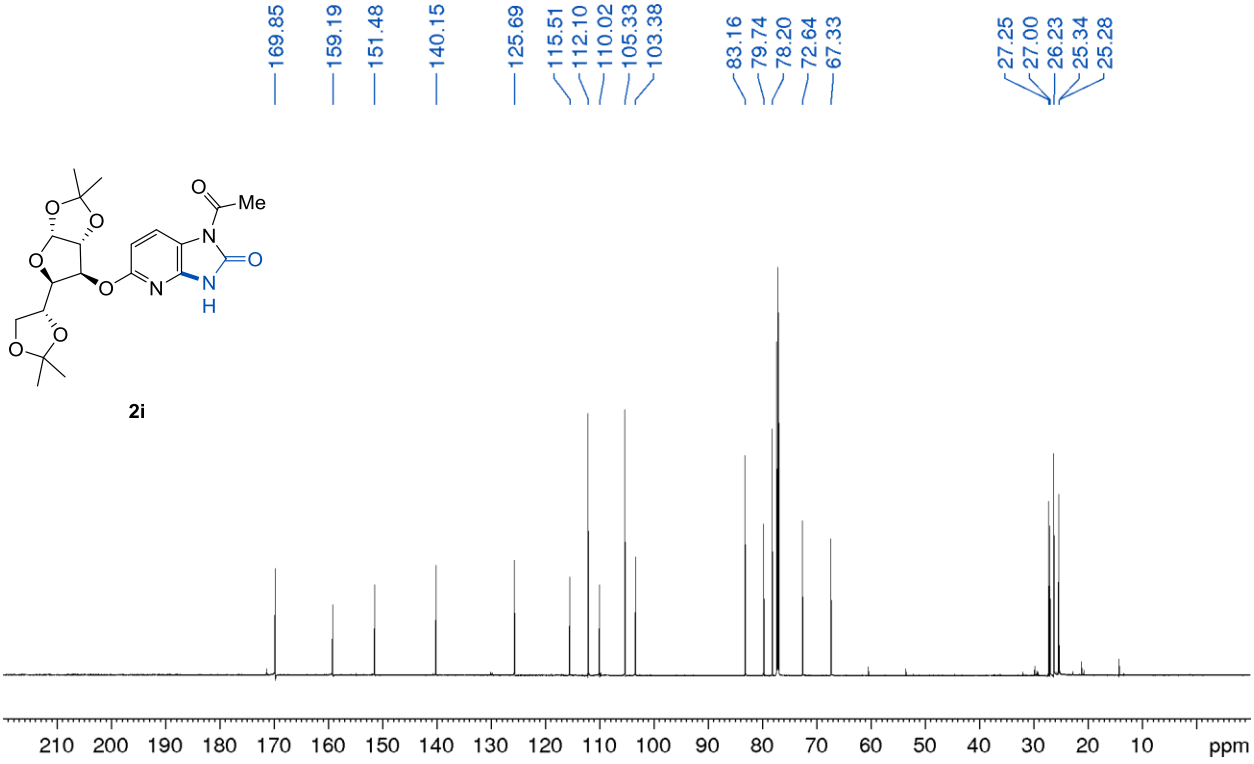
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2h)



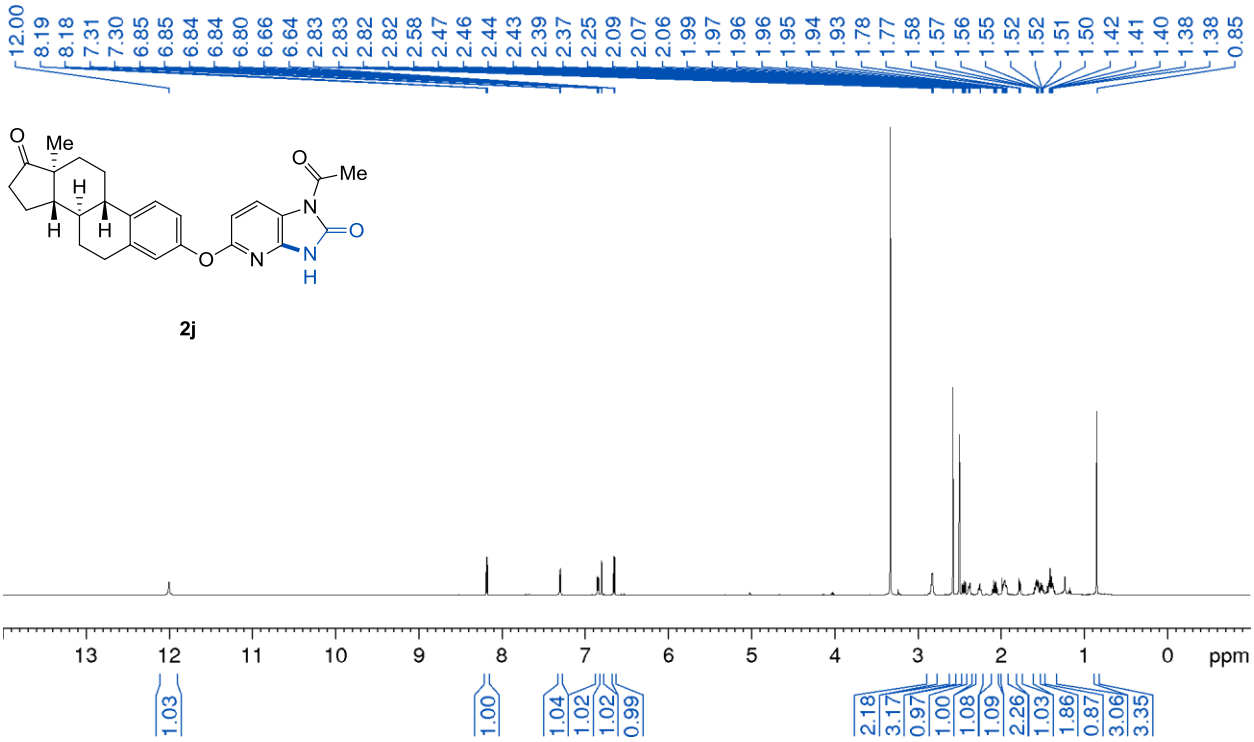
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (2i)



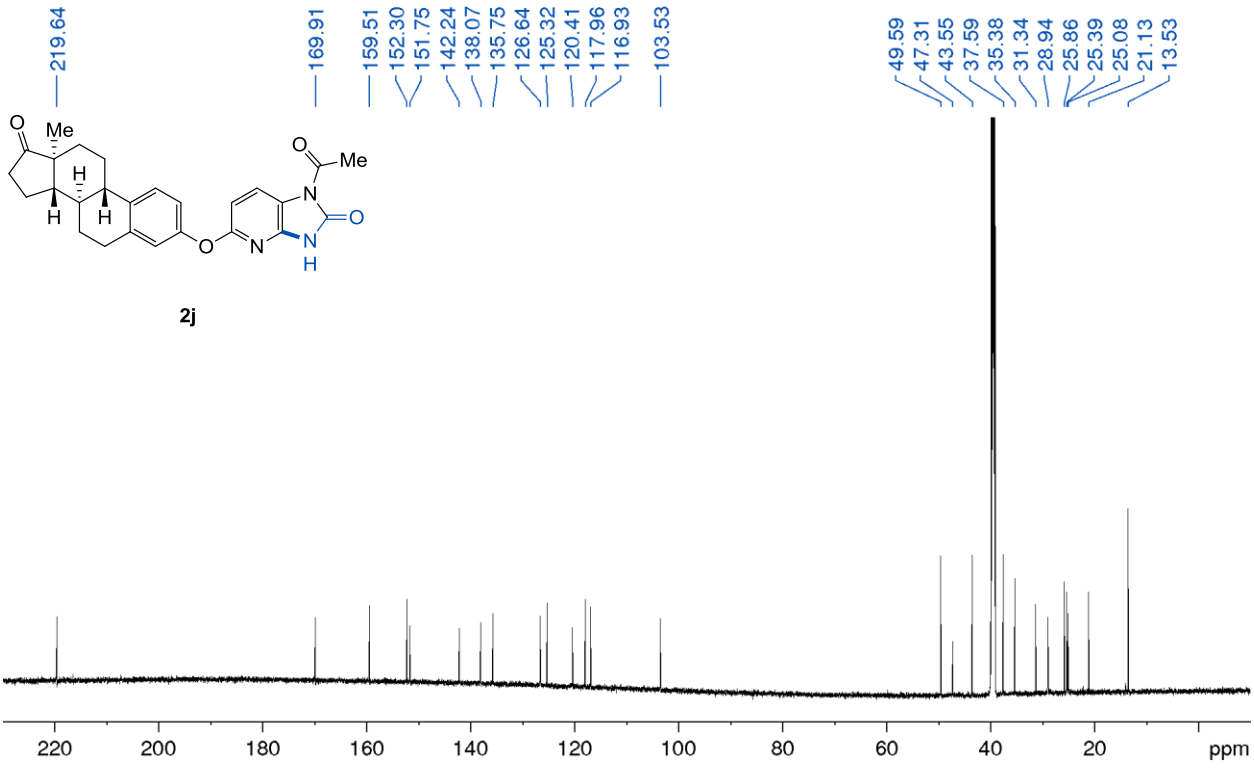
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (2i)



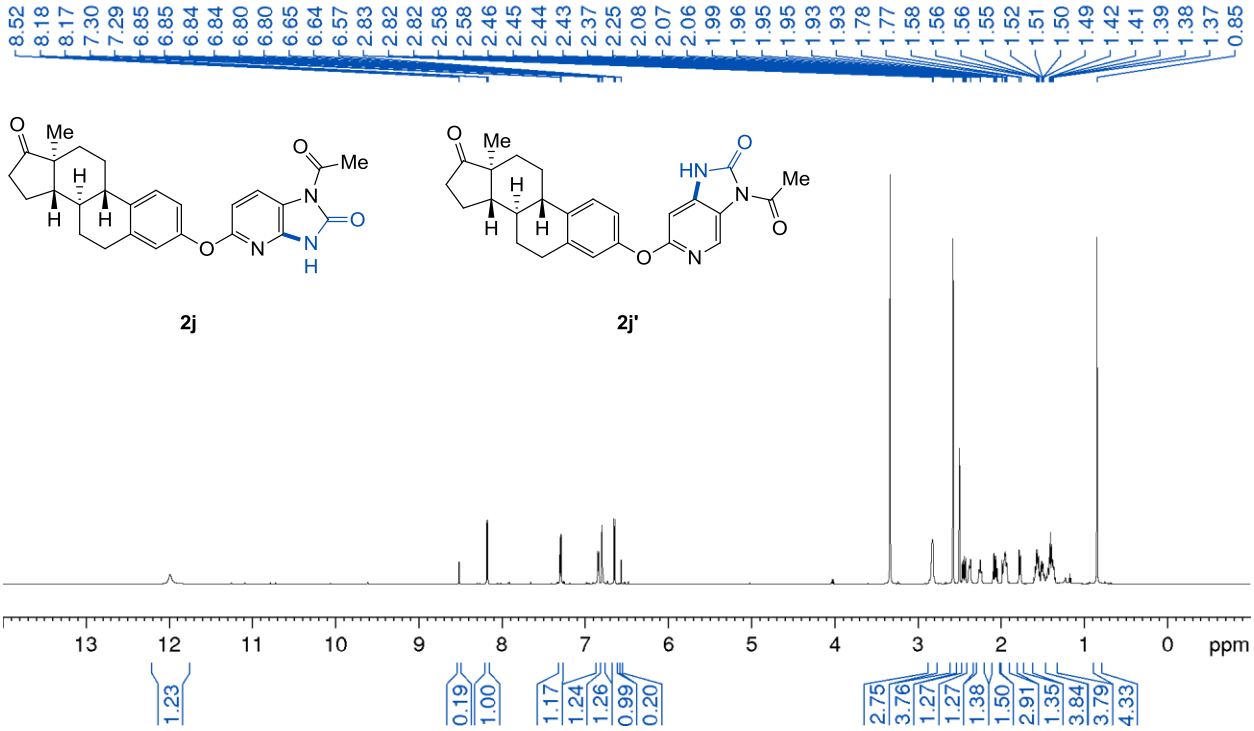
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2j)



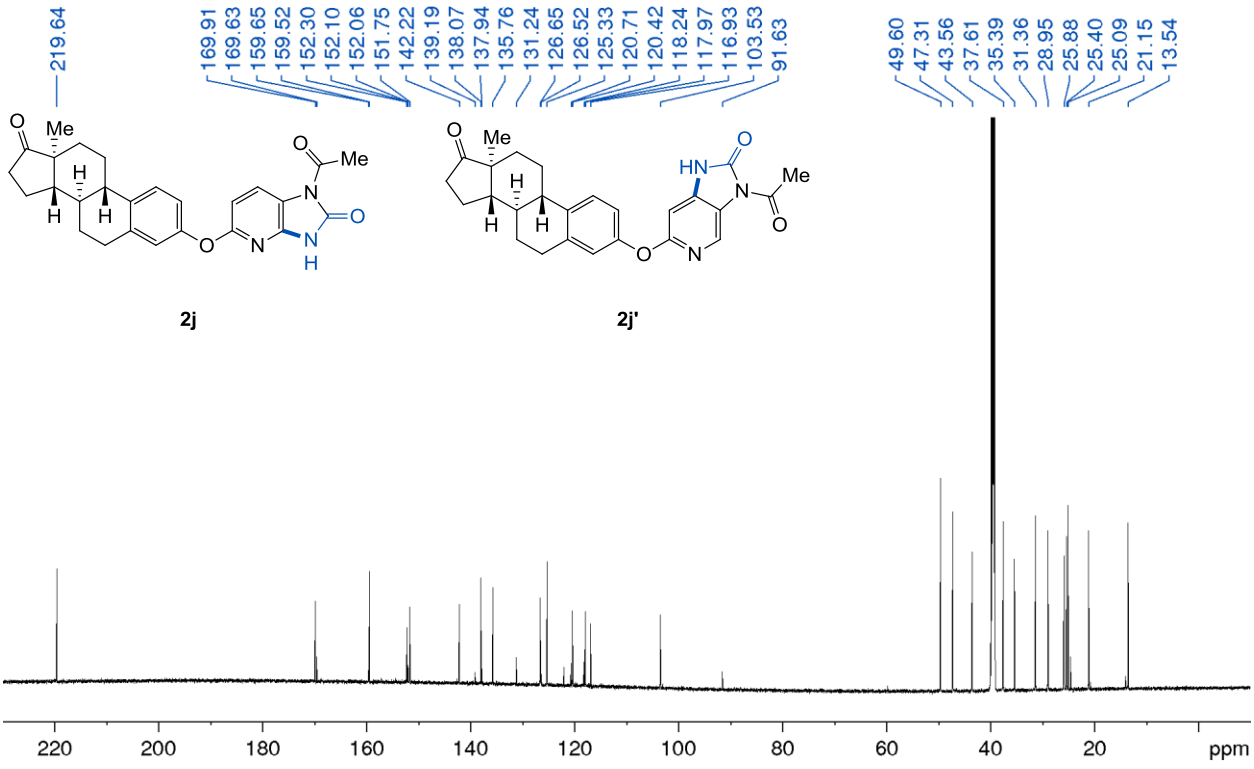
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2j)



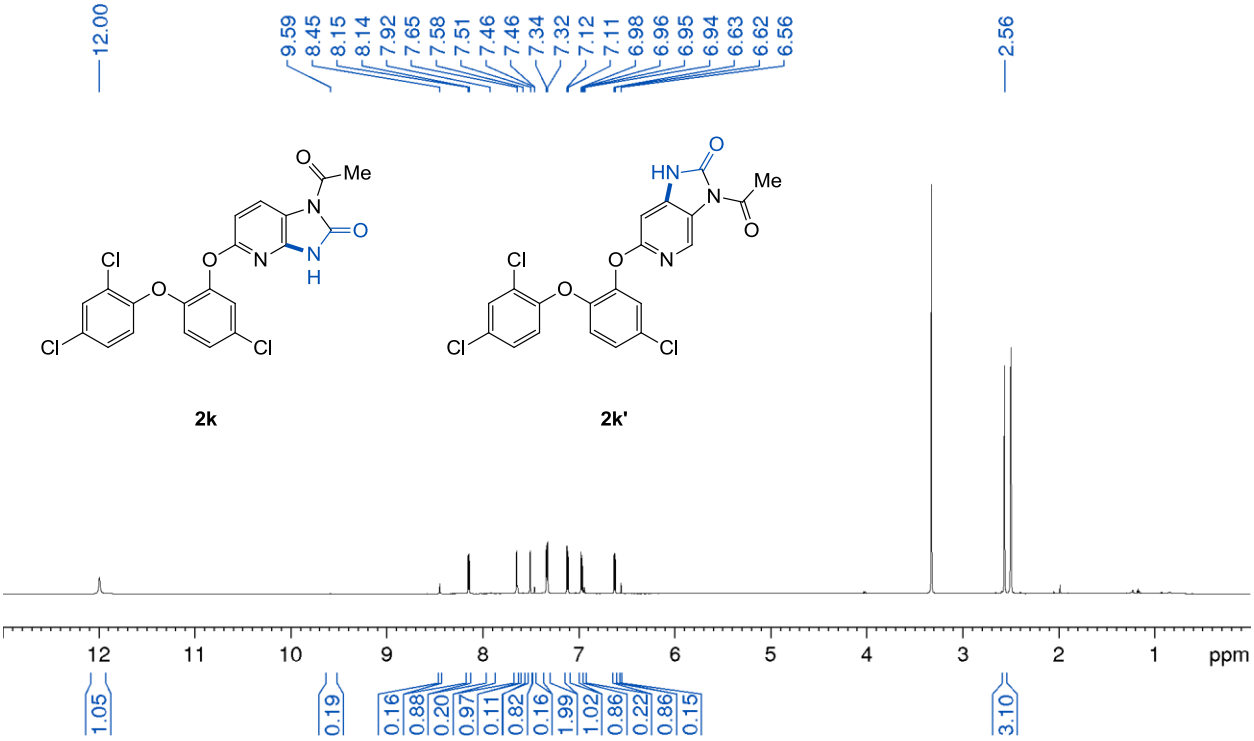
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (2j and 2j')



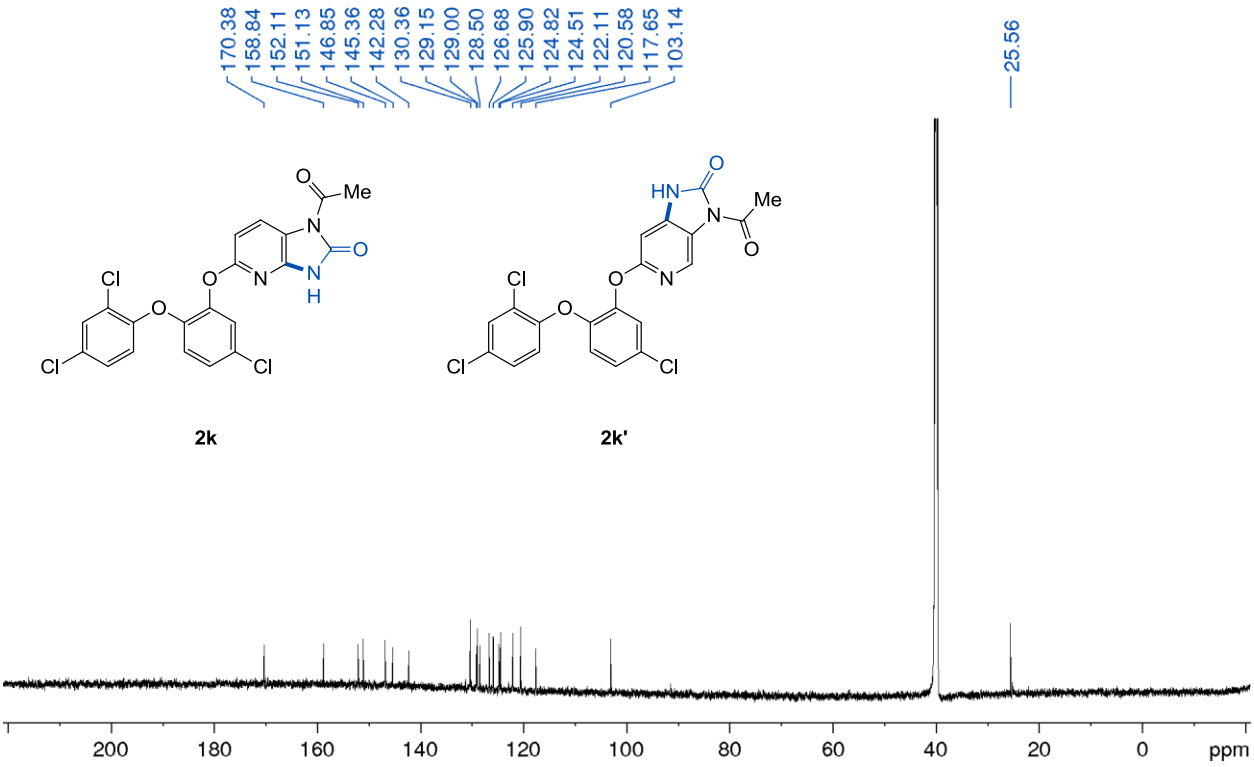
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (2j and 2j')



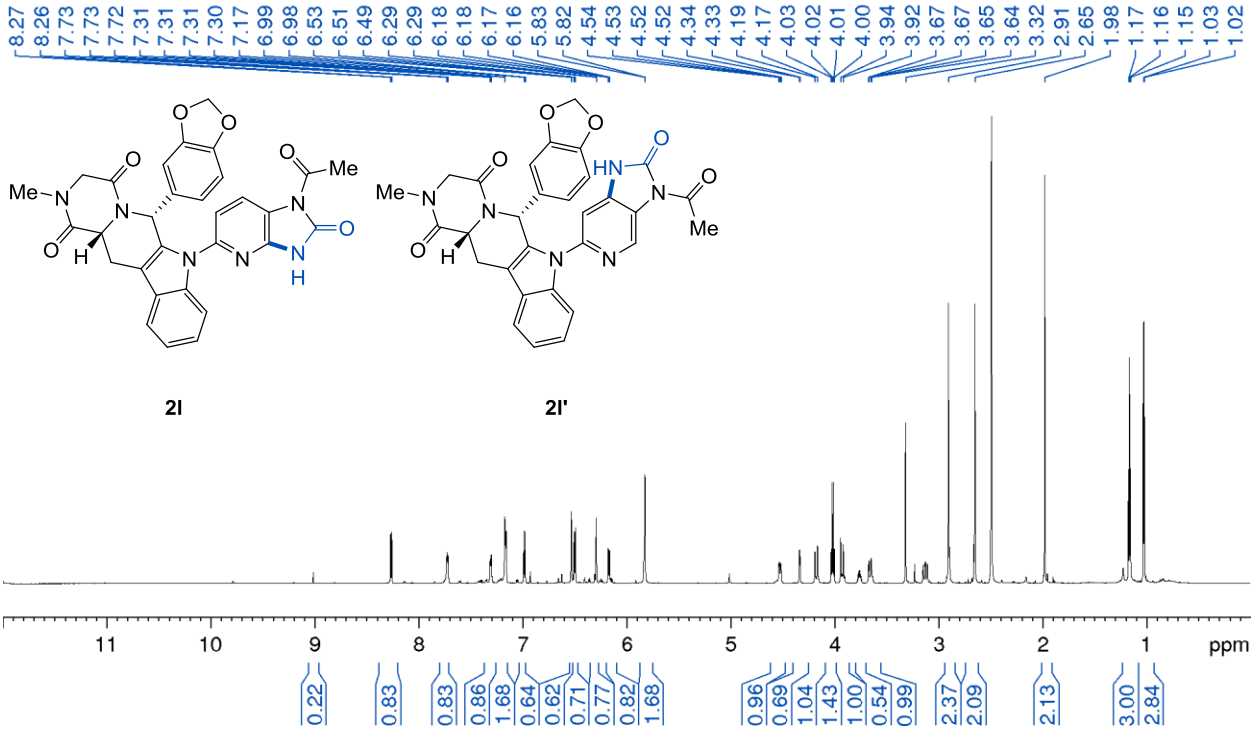
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of (2k and 2k')



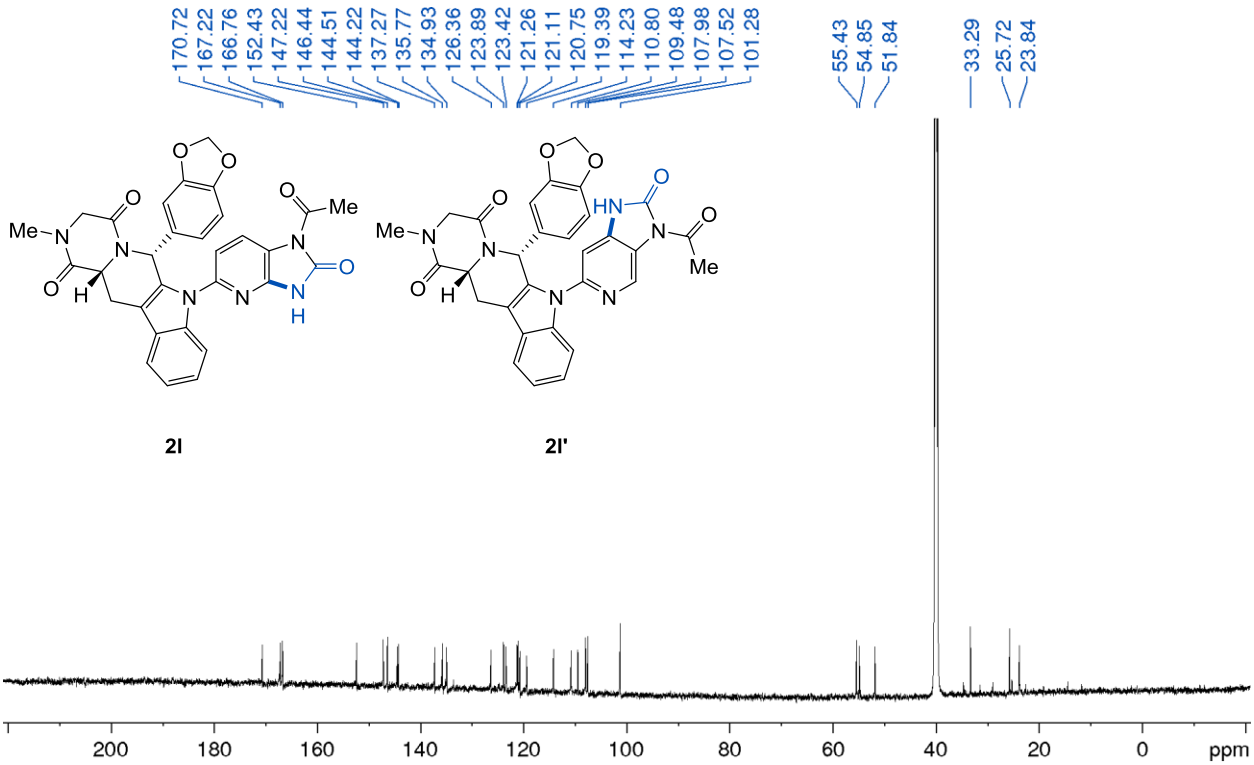
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 ºC) of (2k and 2k')



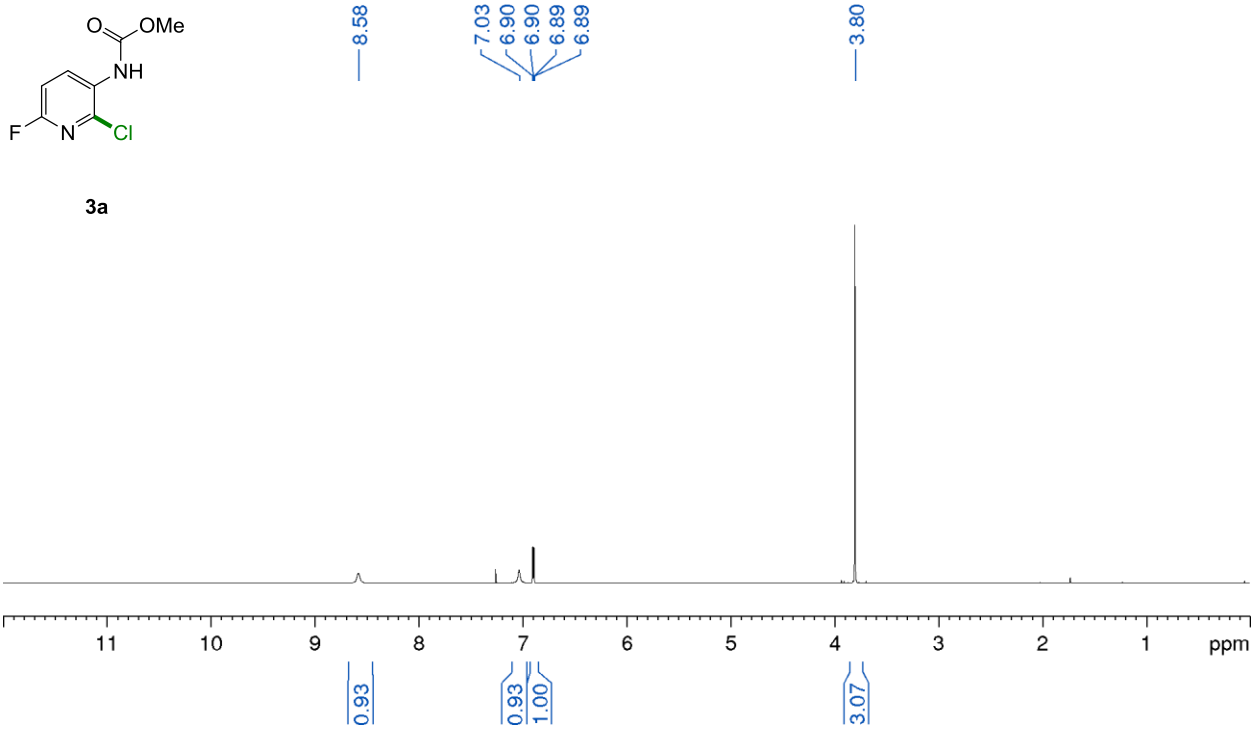
^{1}H NMR (700 MHz, $(CD_3)_2SO$, 25 °C) of (2l and 2l')



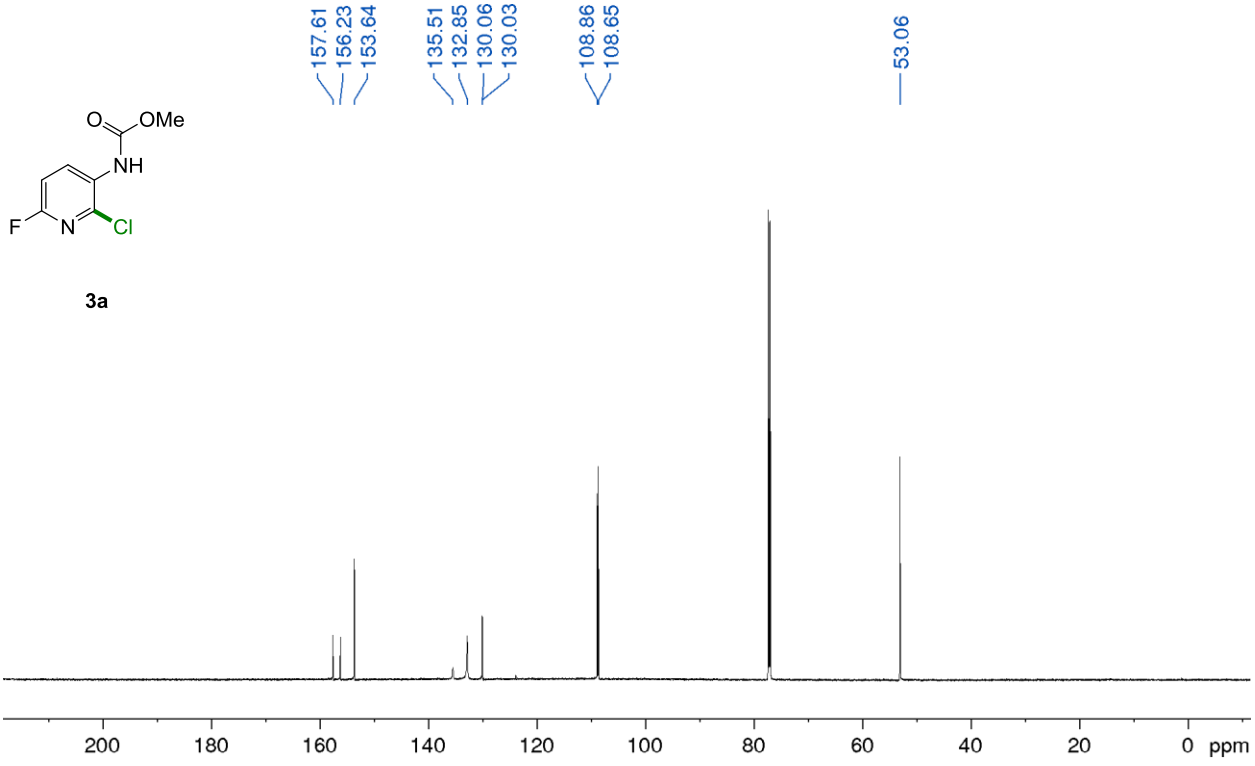
^{13}C NMR (175 MHz, $(CD_3)_2SO$, 25 °C) of (2l and 2l')



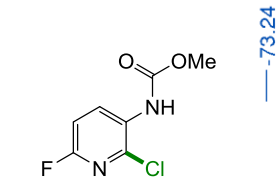
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3a)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3a)

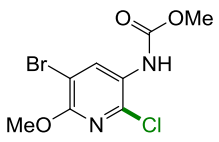


^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3a)



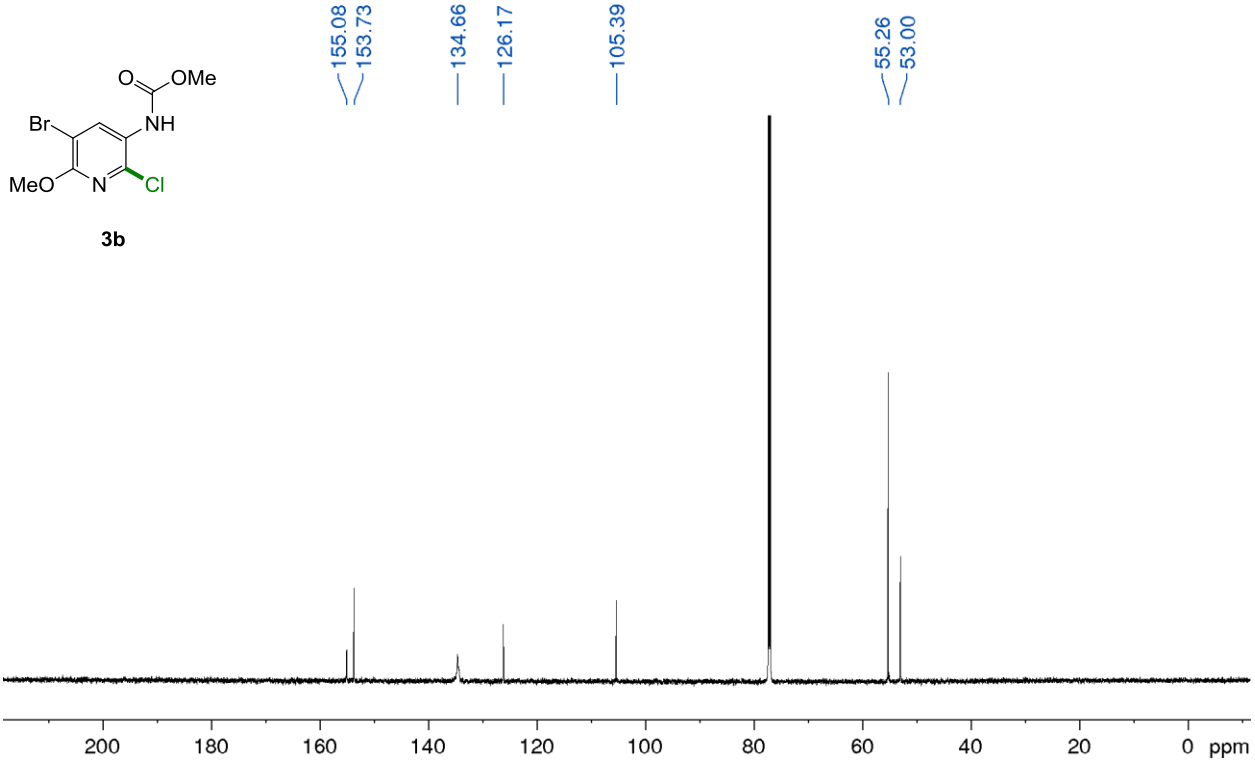
3a

^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3b)

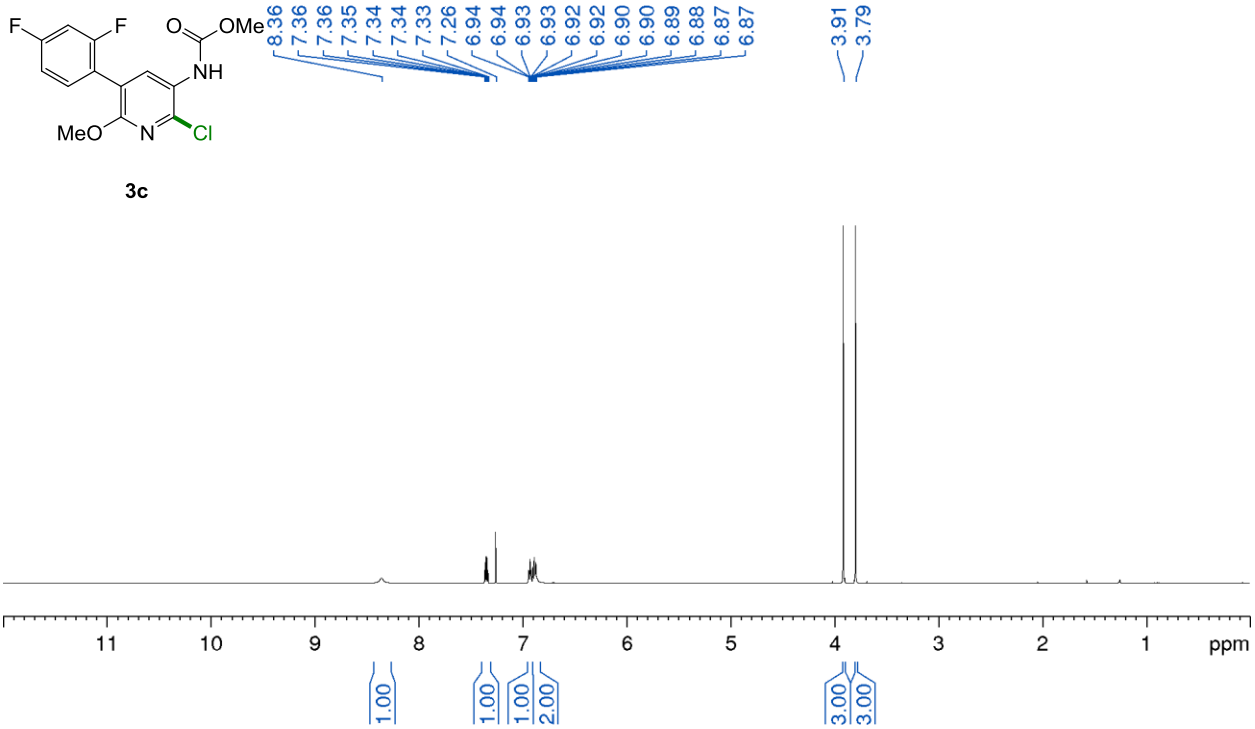


3b

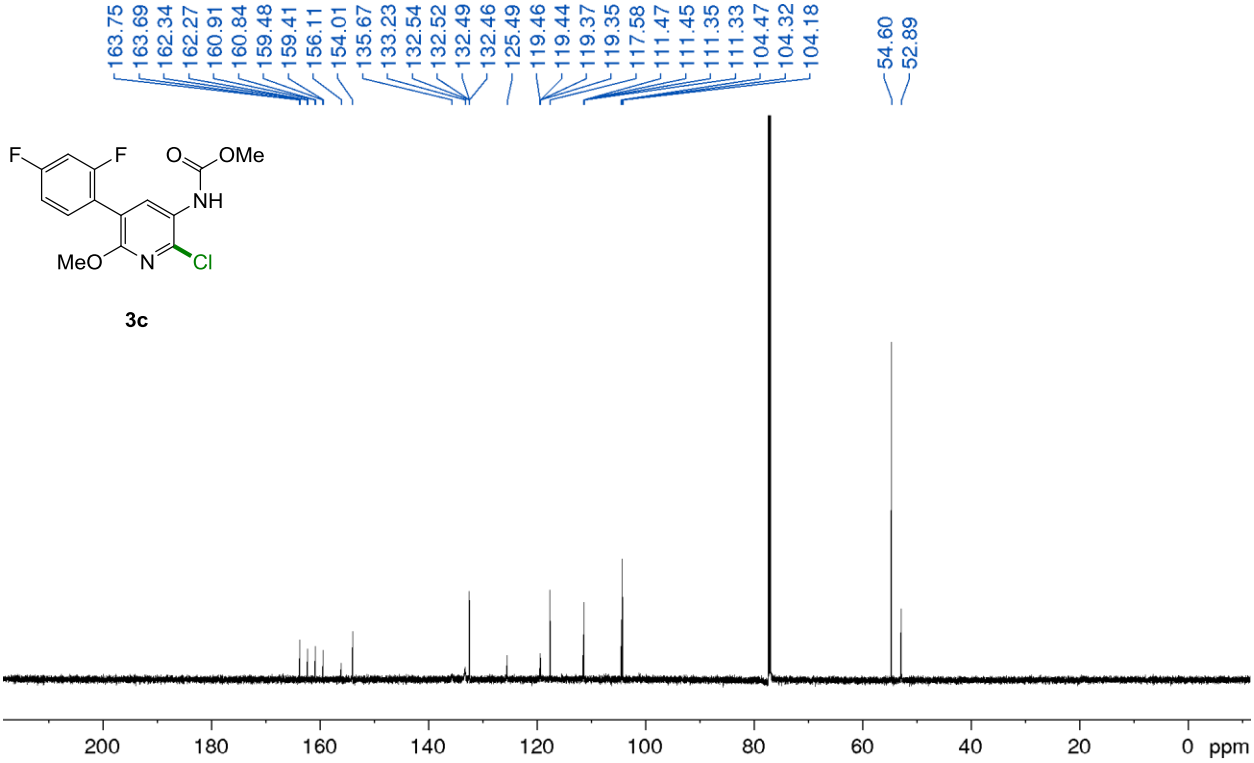
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3b)



^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3c)

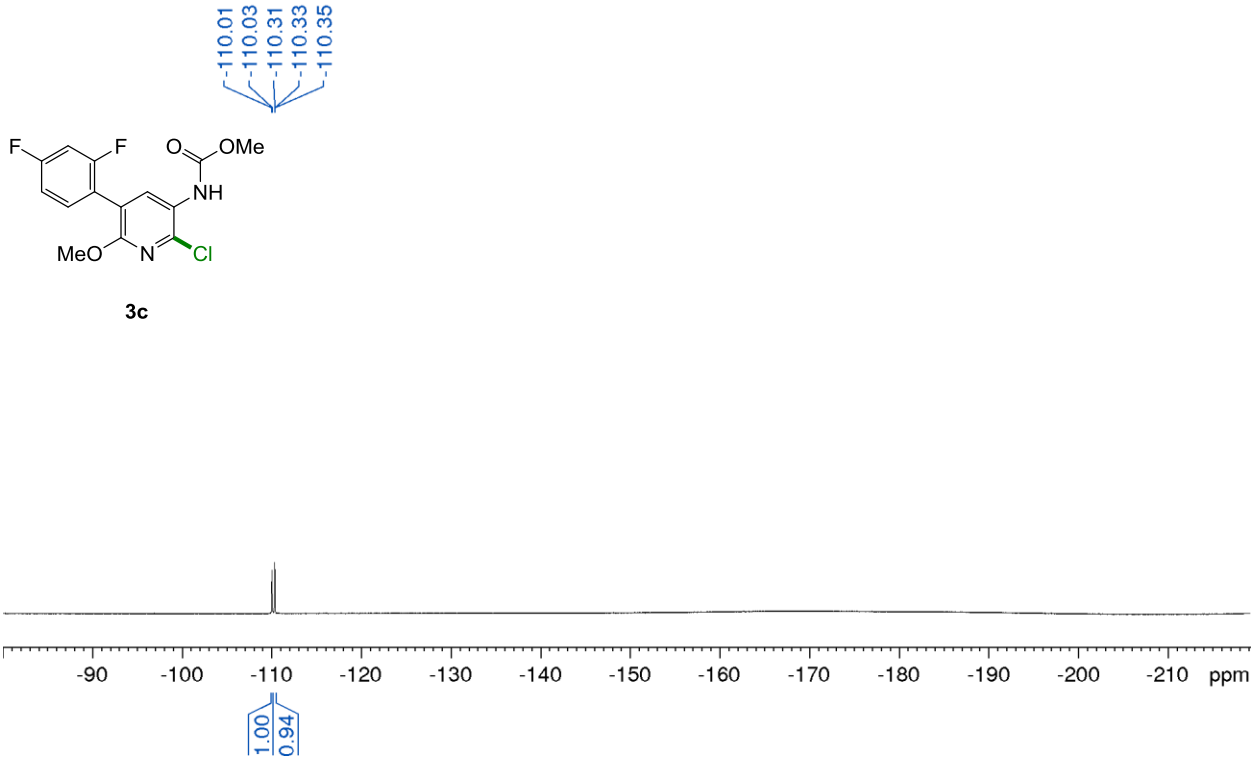


^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3c)



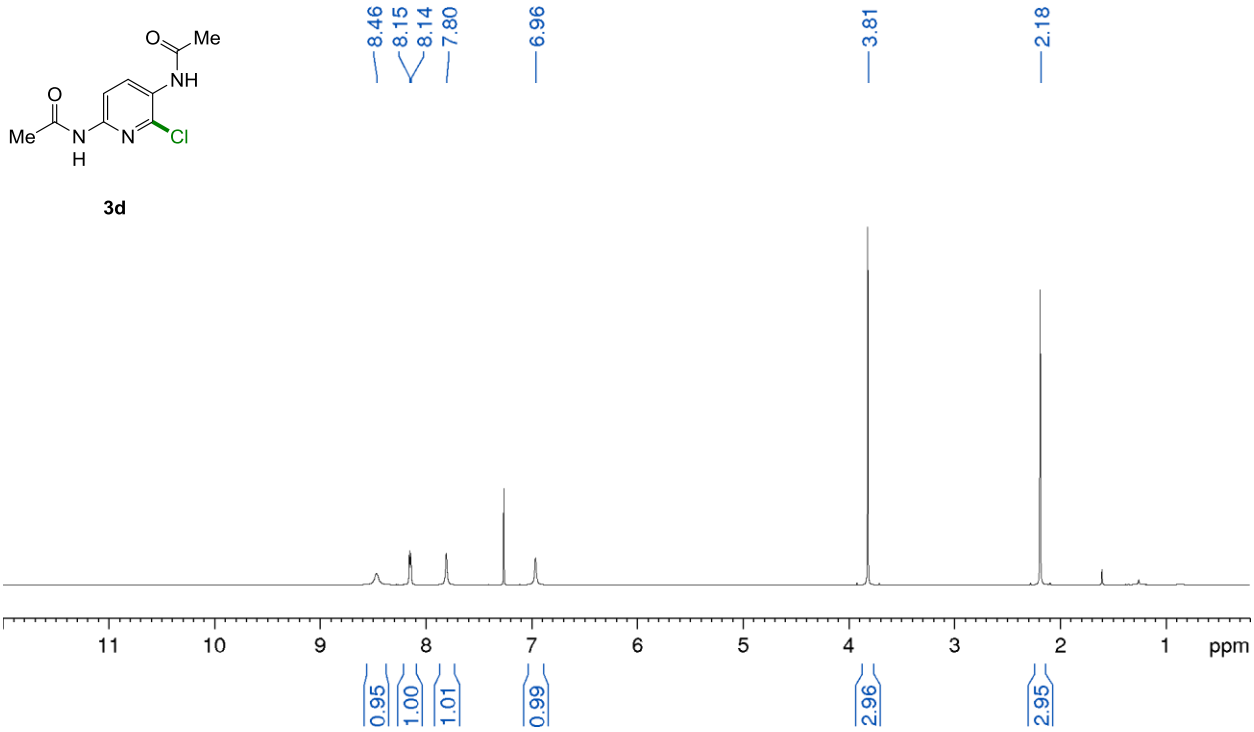
3c

^{19}F NMR (376 MHz, $CDCl_3$, 25 °C) of (3c)



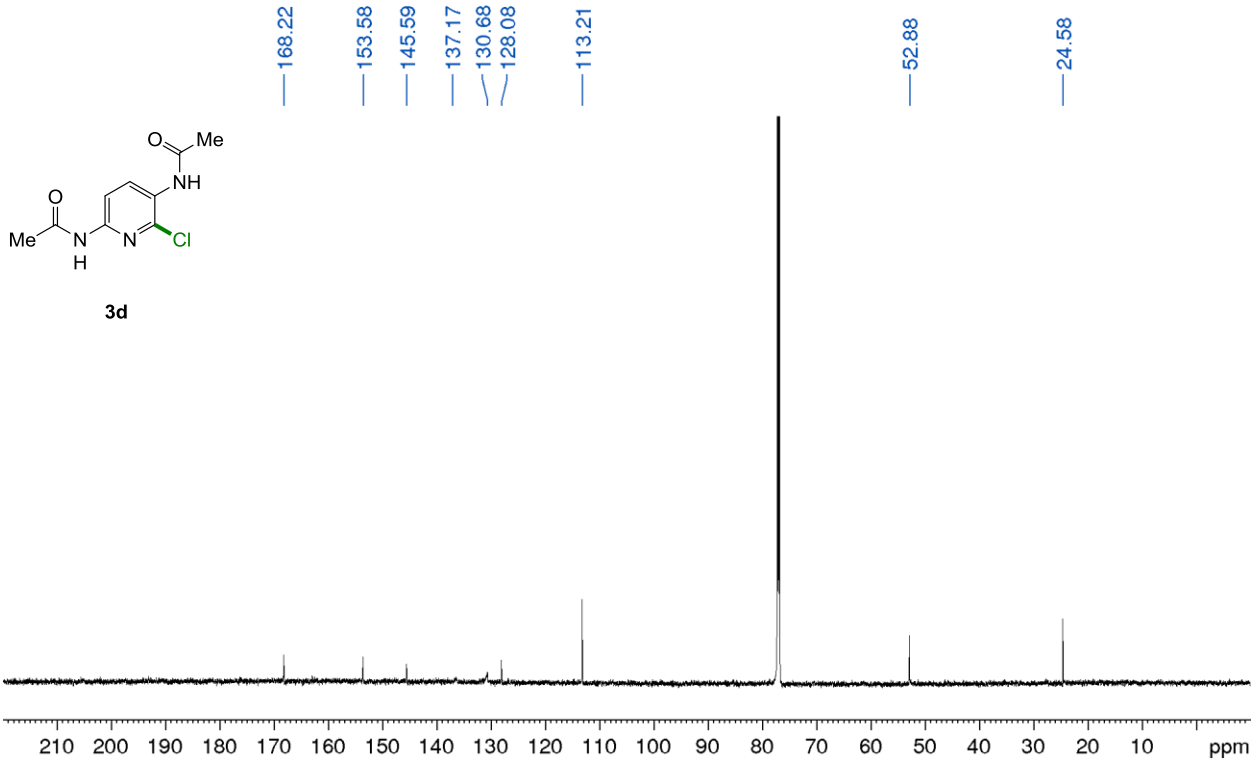
3c

^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3d)



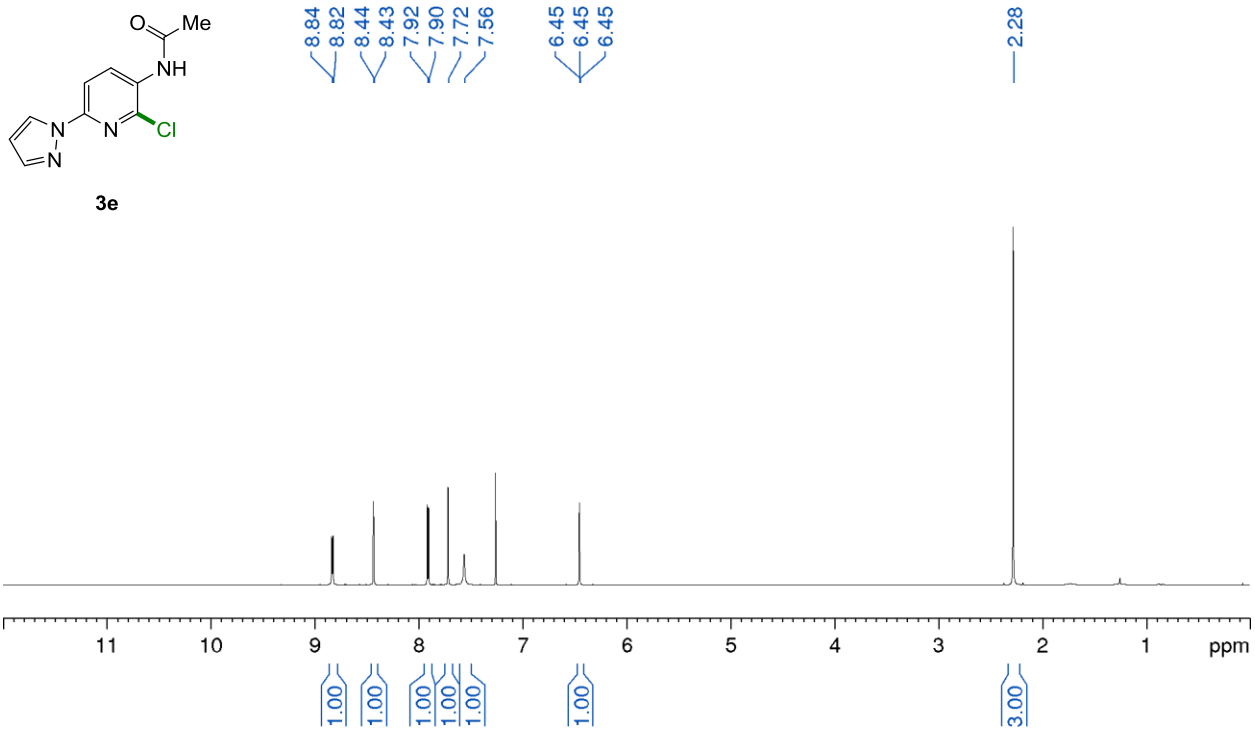
3d

^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3d)

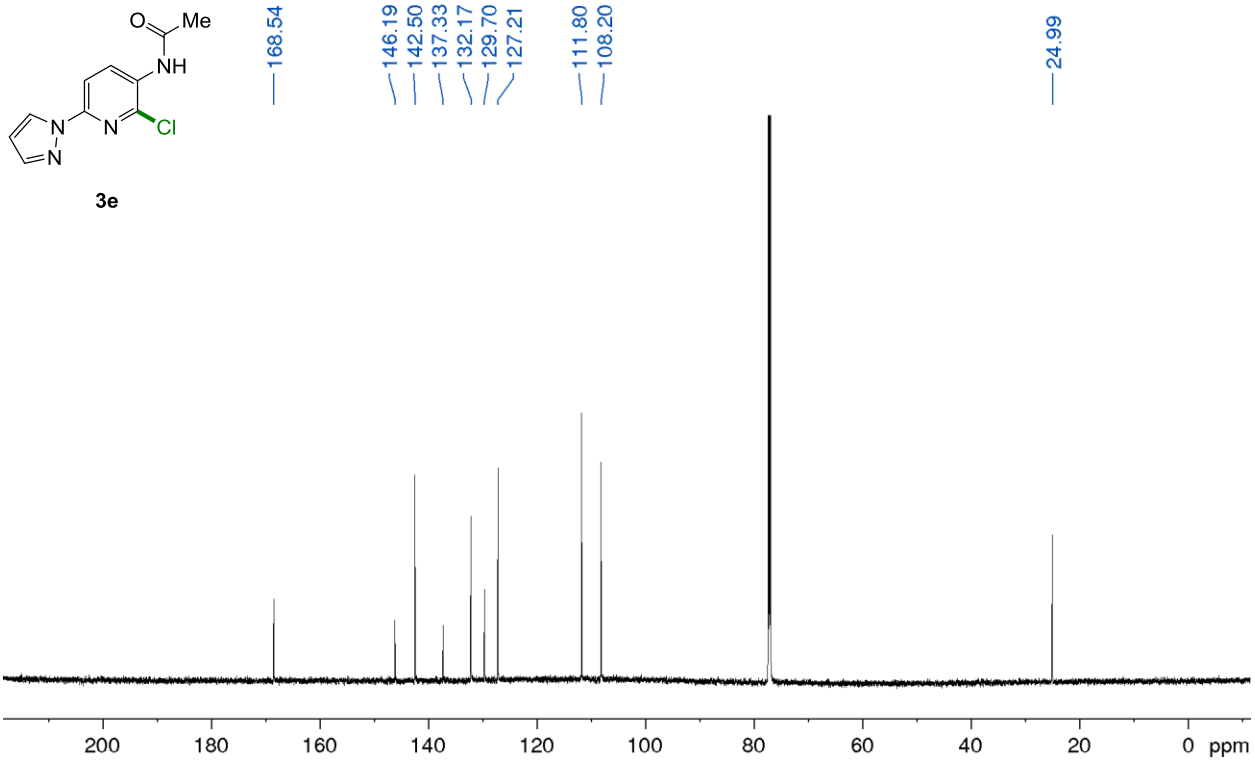


3d

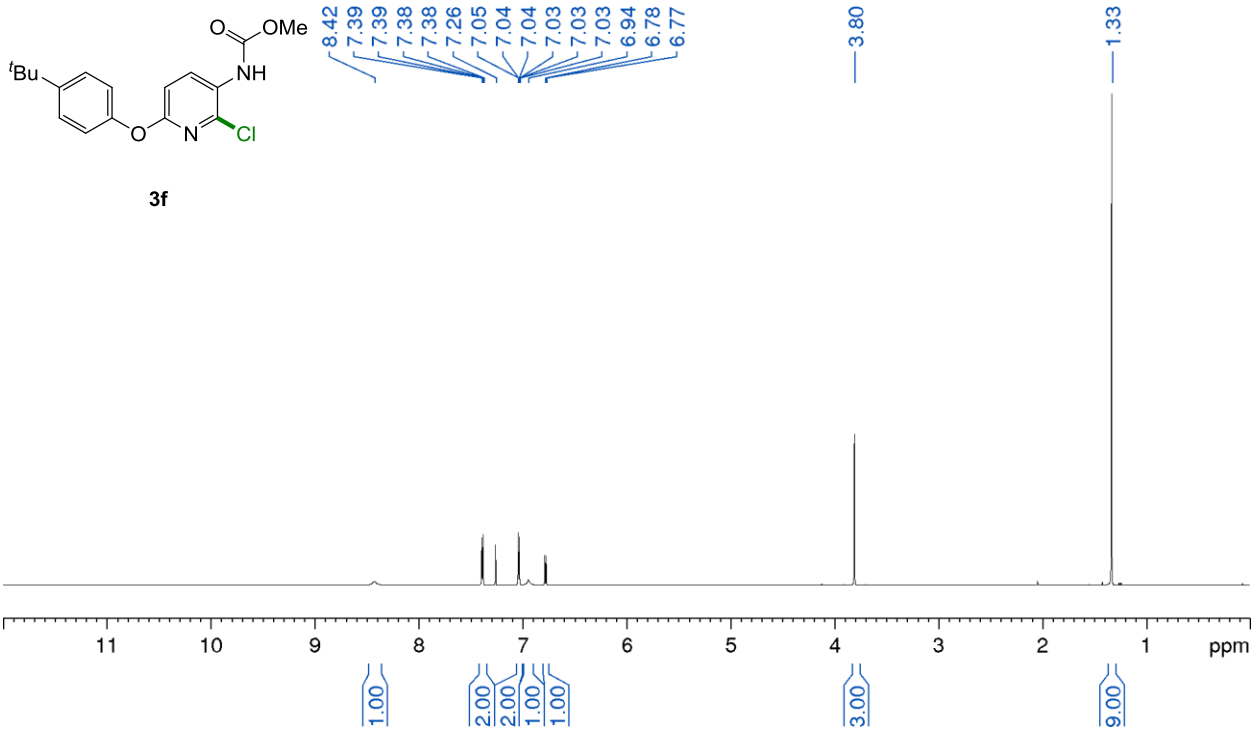
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3e)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3e)

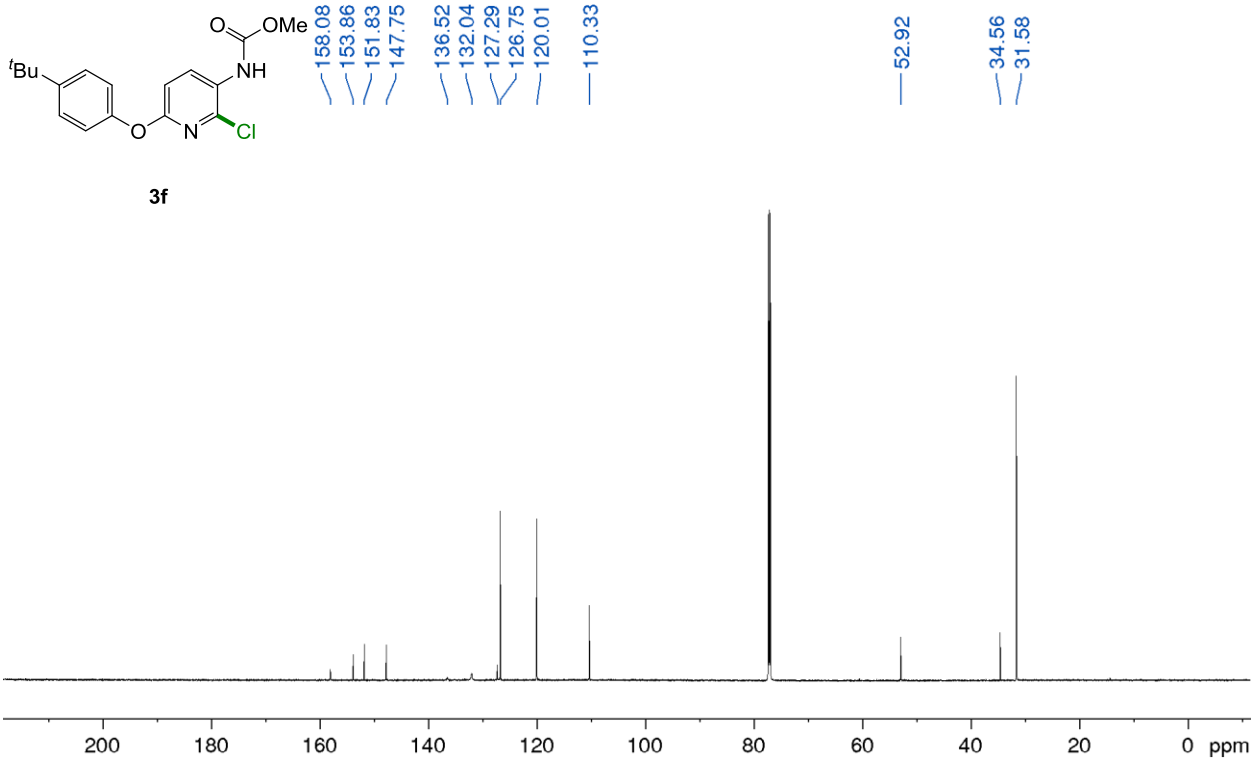


^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3f)



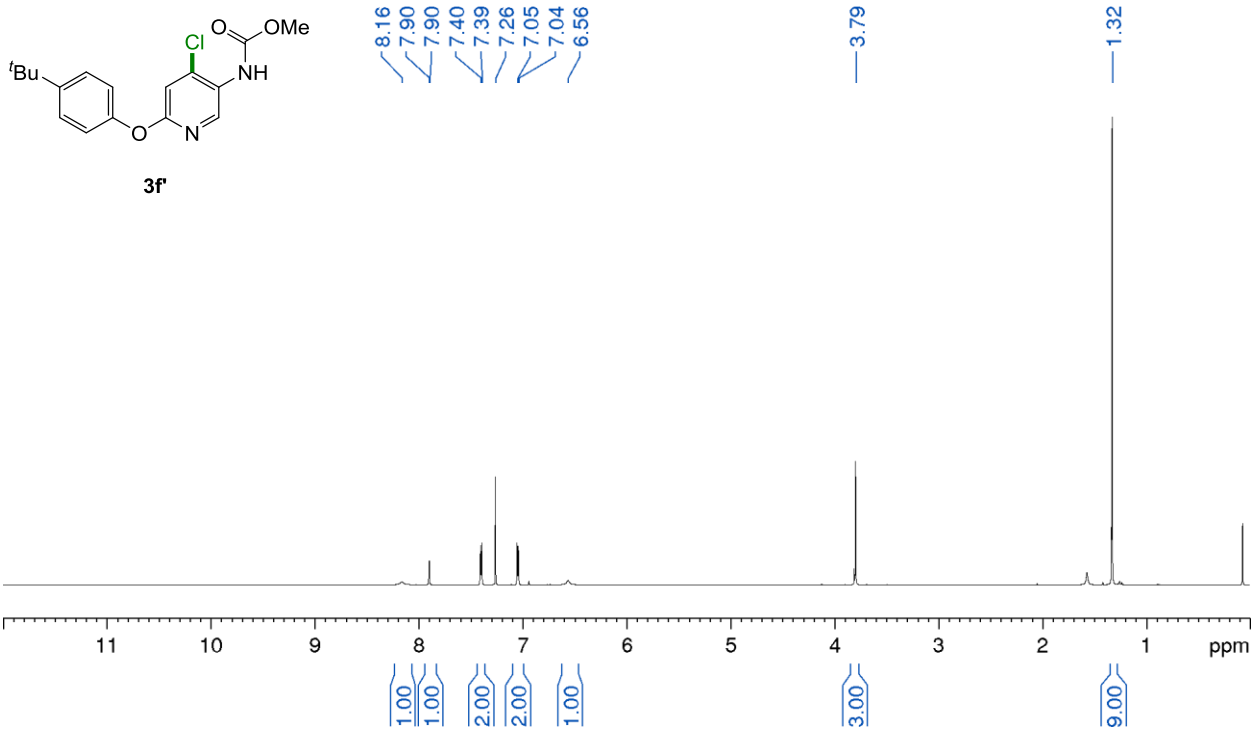
3f

^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3f)

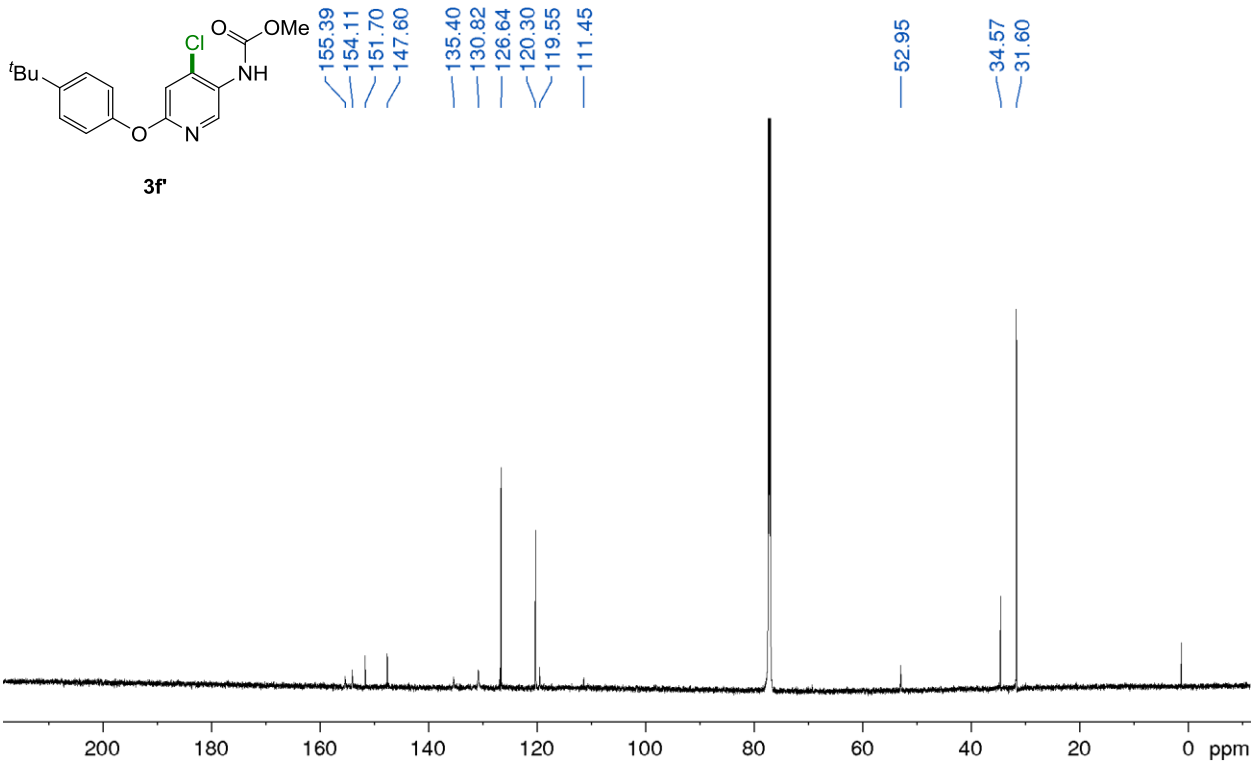


3f

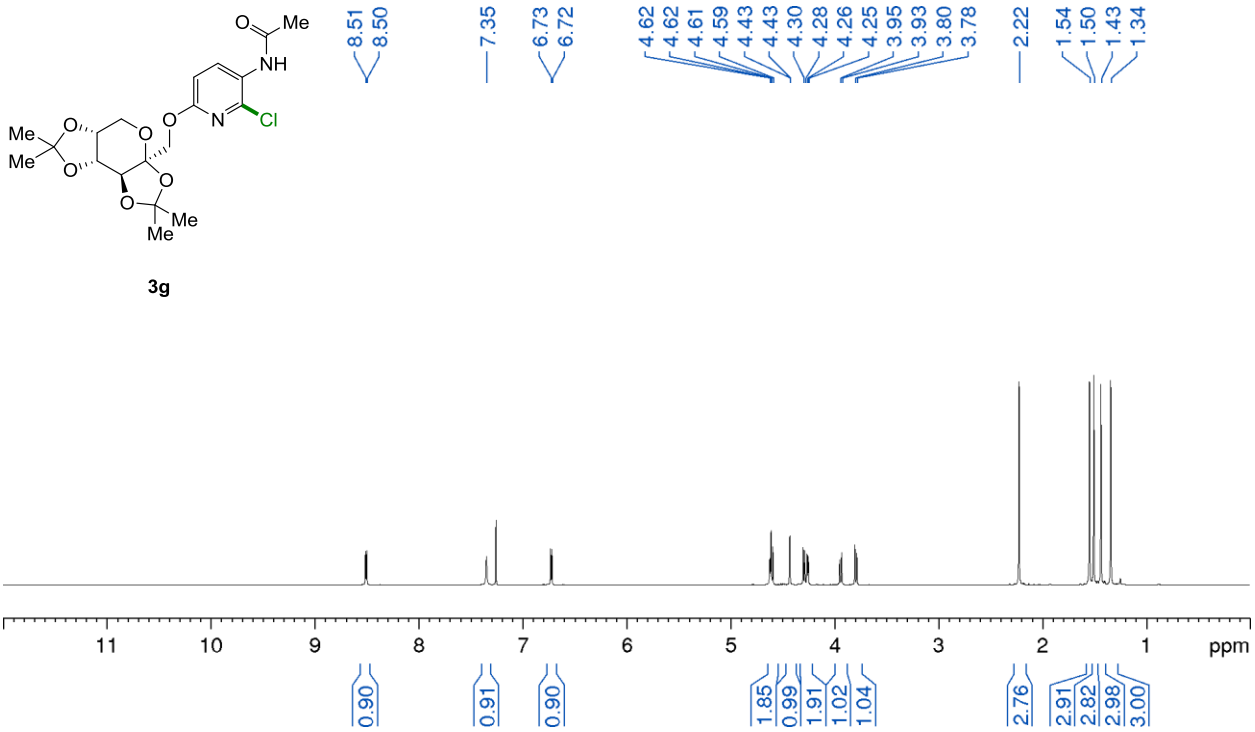
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3f')



^{3}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3f')

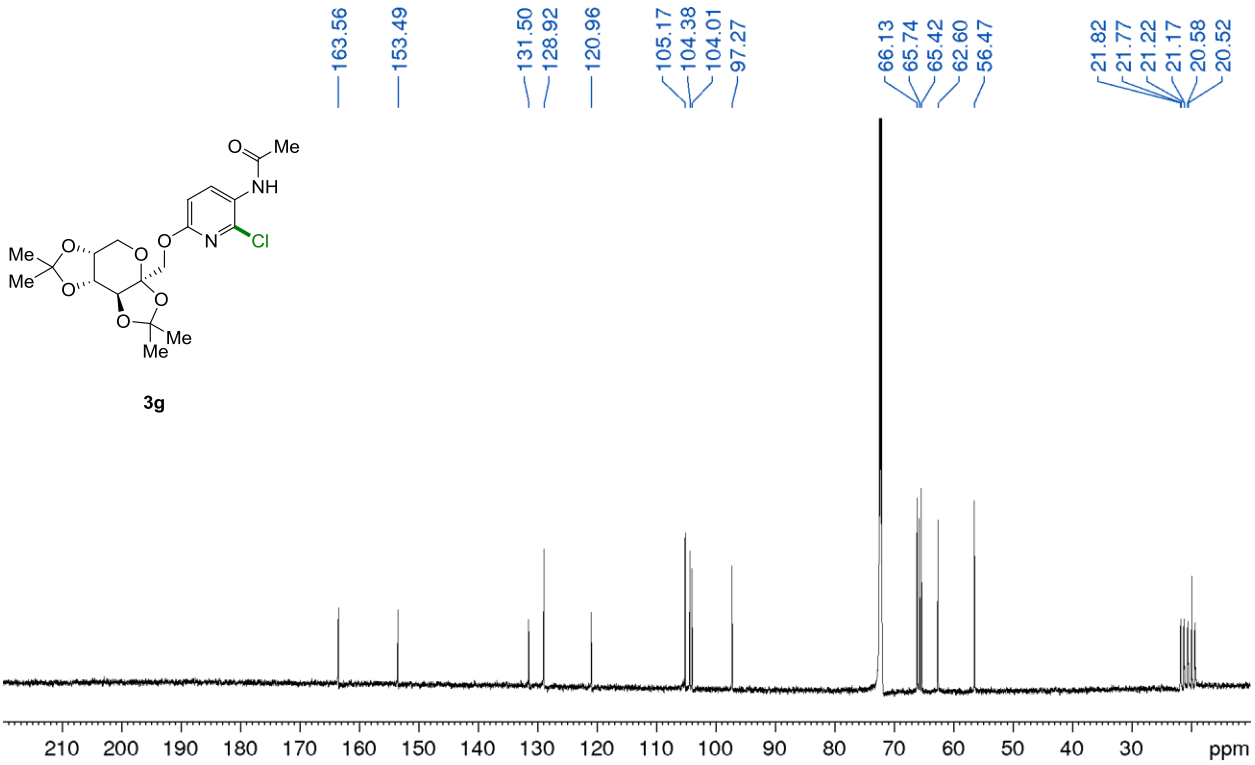


^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3g)



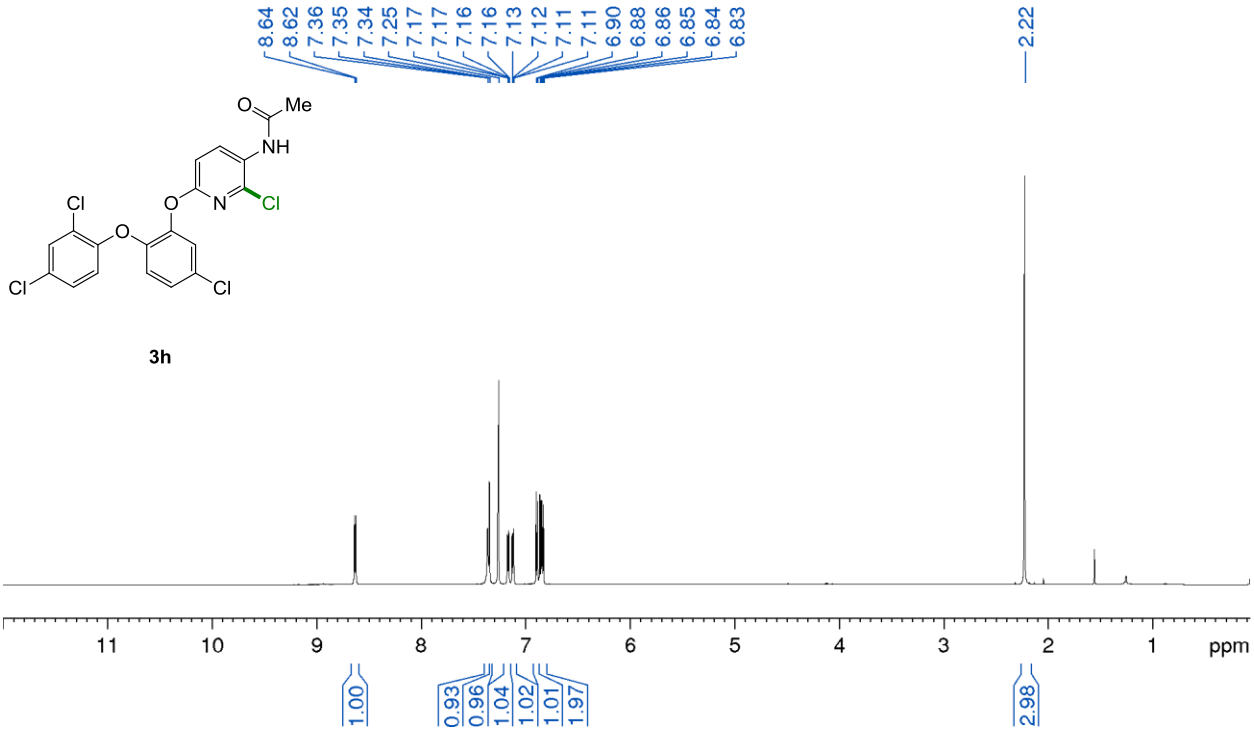
3g

^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3g)

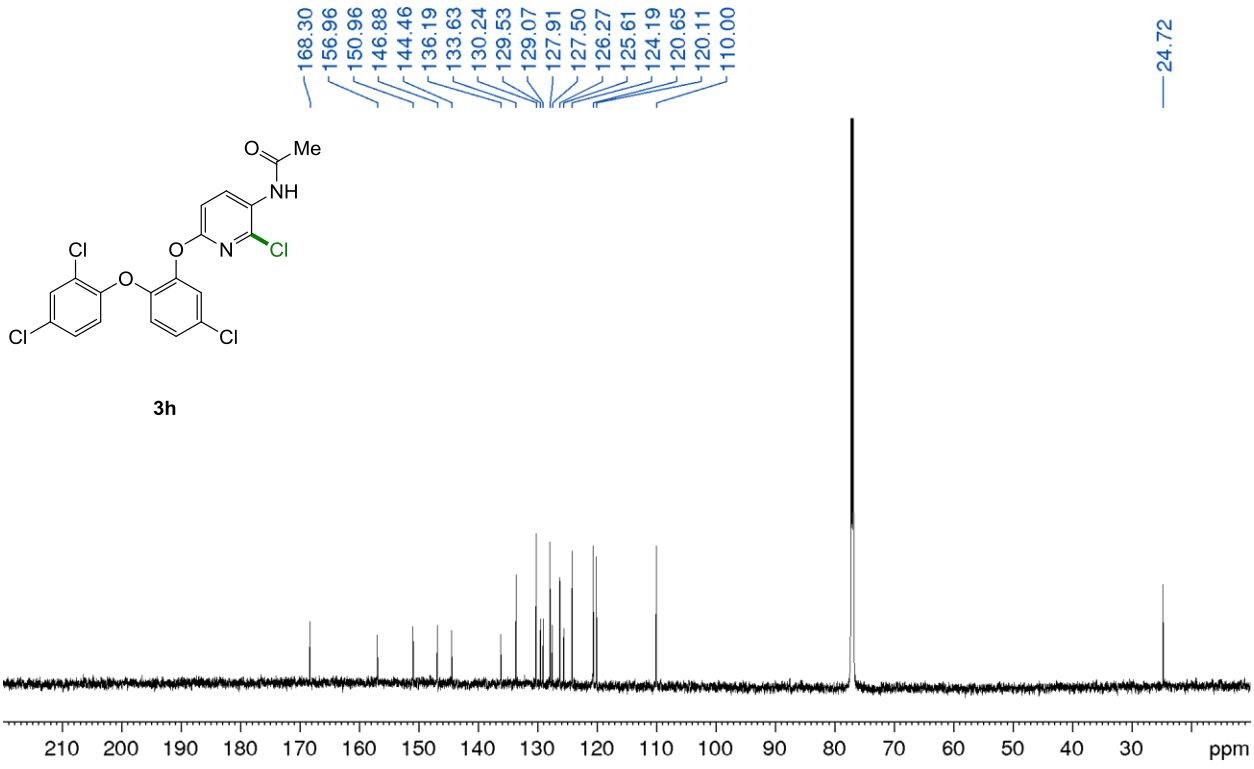


3g

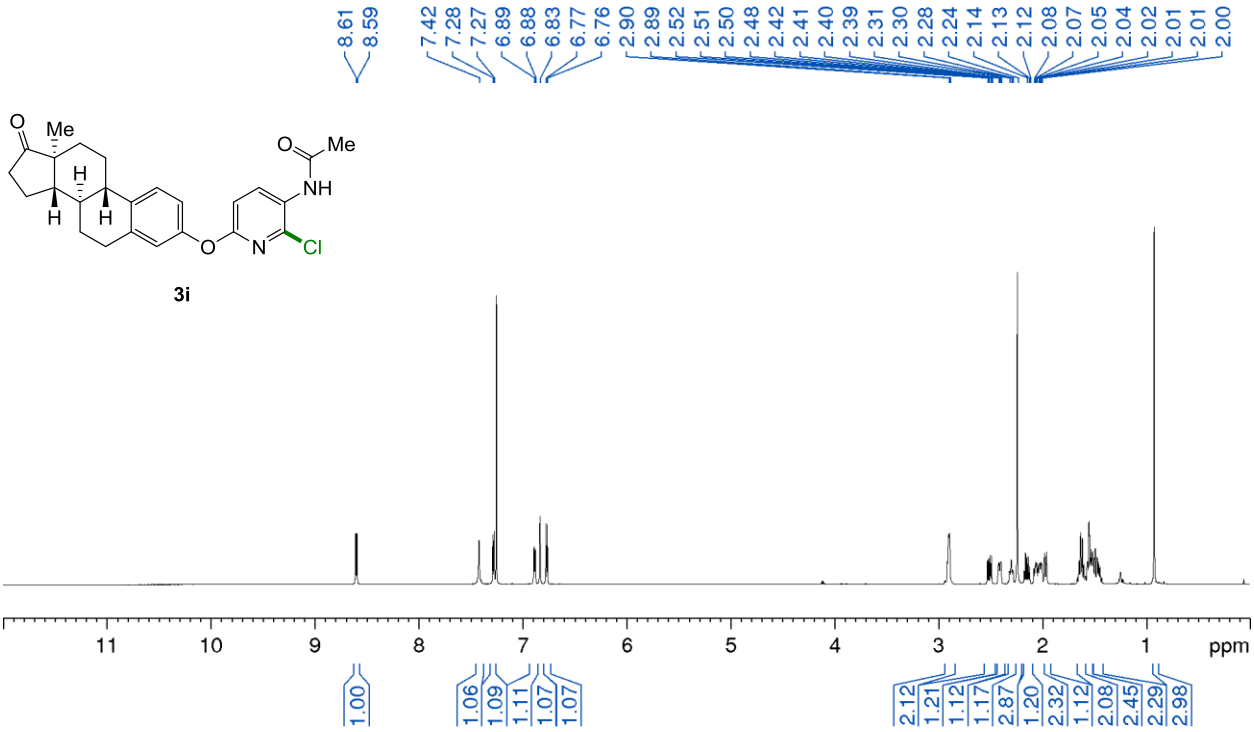
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3h)



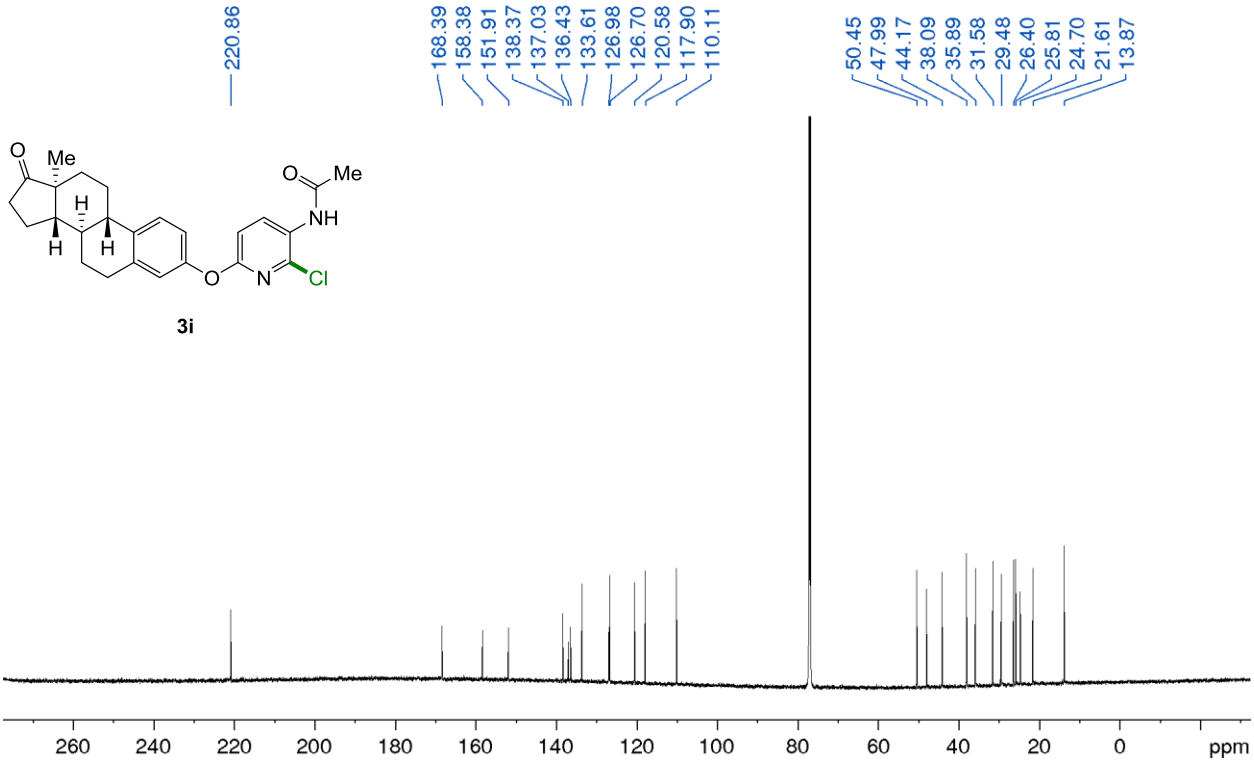
^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3h)



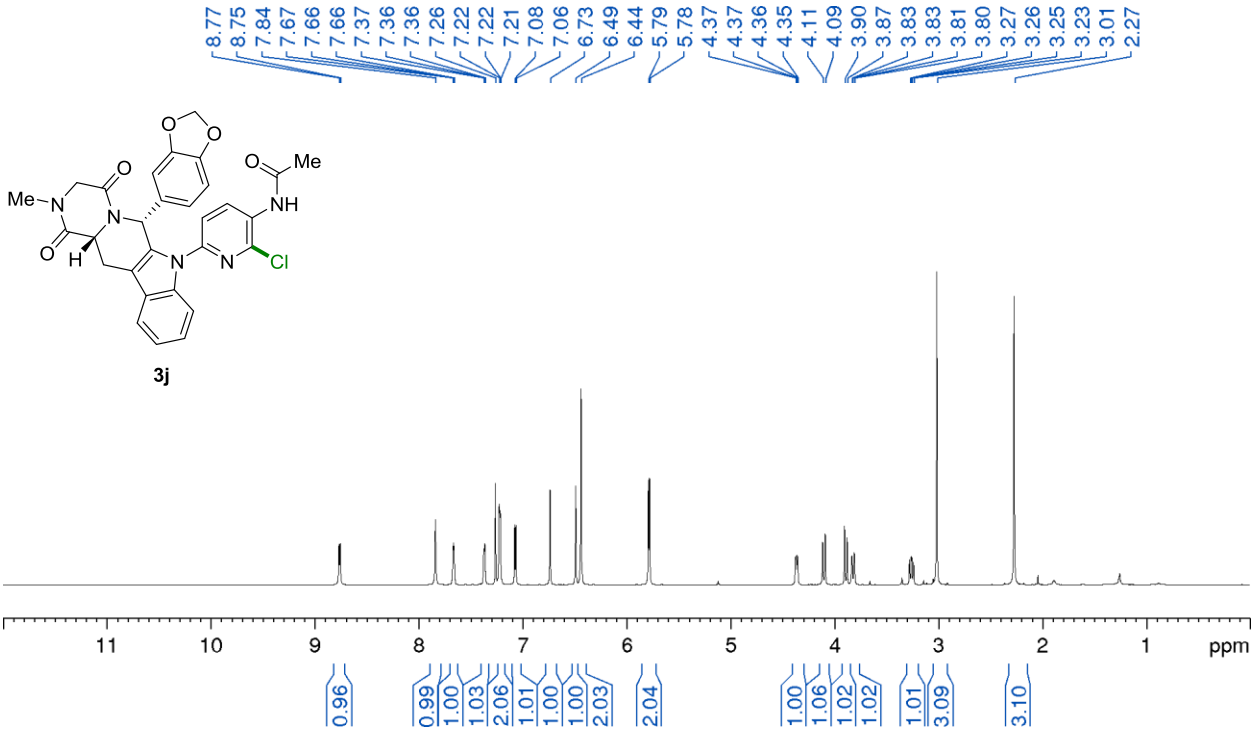
^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3i)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3i)



^{1}H NMR (700 MHz, $CDCl_3$, 25 °C) of (3j)



^{13}C NMR (175 MHz, $CDCl_3$, 25 °C) of (3j)