# Supporting Information

# *β*-Selective Reductive Coupling of Alkenylpyridines with Aldehydes and Imines via Synergistic Lewis Acid/Photoredox Catalysis

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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 under UV light. The photoredox reactions were performed using 30 W blue LED light purchased online from babaoshop (an ebay vendor). Flash chromatography was performed on SiliaFlash® Silica Gel 40-63μm 60Å particle size.[1] All air- and moisture-sensitive manipulations were performed using oven-dried glassware, including standard Schlenk and glovebox techniques under an atmosphere of nitrogen. Diethyl ether and THF were distilled from deep purple sodium benzophenone ketyl. Methylene chloride, chloroform and acetonitrile were dried over $CaH_2$ and distilled. All purchased liquid substrates that were purchased were distilled and subject to 3 cycles of freeze-pump-thaw prior to being used for the coupling reactions. 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 176 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, a Bruker 400 Nanobay spectrometer operating at 400 MHz, 100 MHz, and 376 MHz for $^{1}H$, $^{13}C$, and $^{19}F$ acquisitions, or a Bruker 300 MHz Ultra-Shield Fourier spectrometer operating at 300 MHz, 75 MHz MHz for $^{1}H$, and $^{13}C$ 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; $CD_3OD$, δ 3.31; $CD_3CN$, δ 1.94), solvent $^{13}C$ signals ($CDCl_3$, δ 77.16; $(CD_3)_2SO$, δ 39.52; $CD_3OD$, δ 49.00),[2] dissolved or external neat $PhCF_3$ ($^{19}F$, δ –63.3 relative to $CFCl_3$),[3] or *m*-fluoronitrobenzene ($^{19}F$, δ –112.01).[4] Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. High-resolution mass spectra were performed at Mass Spectrometry Services at Stony Brook University and were obtained using Agilent LC-UV-TOF mass spectrometer. Concentration under reduced pressure was performed by rotary evaporation at 25–30 °C 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

## Experimental Setup of the Photoredox Reaction

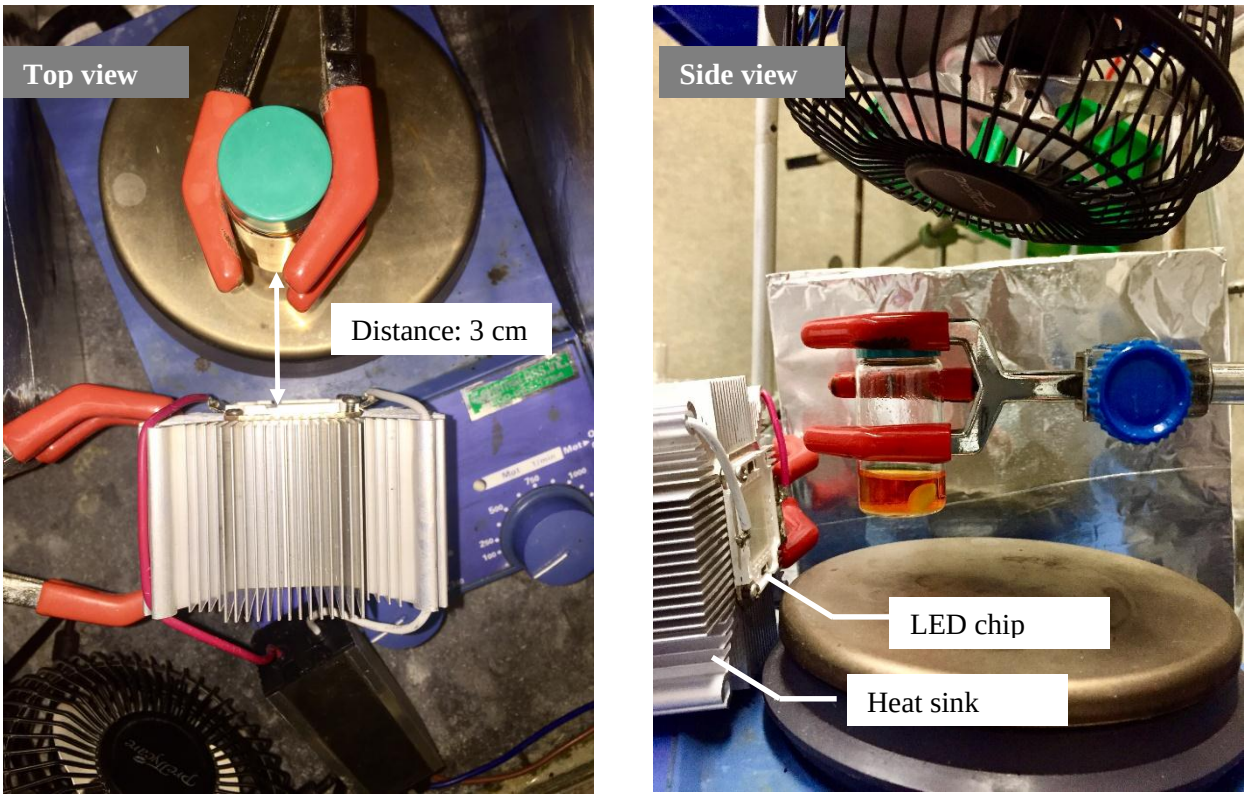



**Figure S1.** Pictures of the experimental setup.

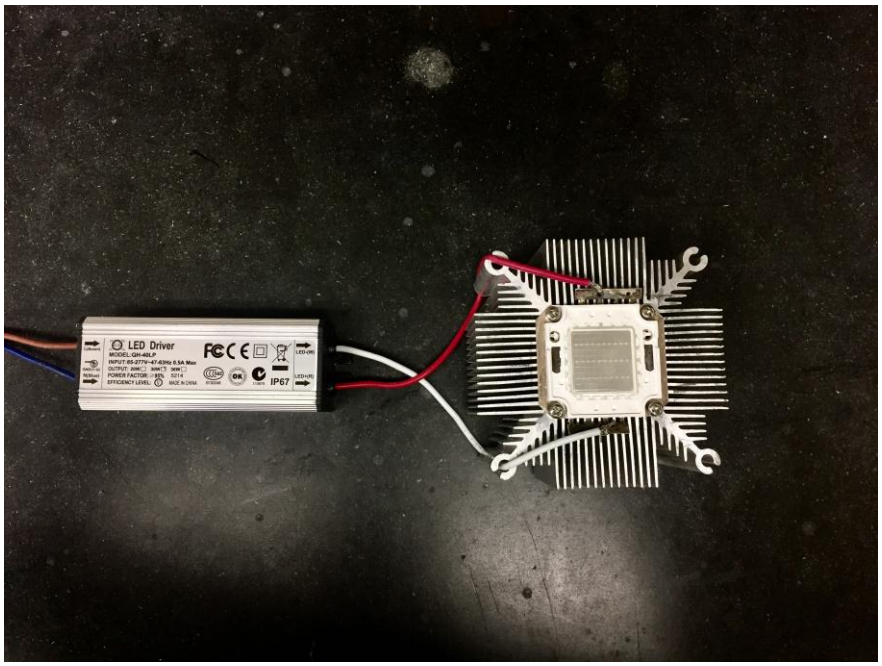
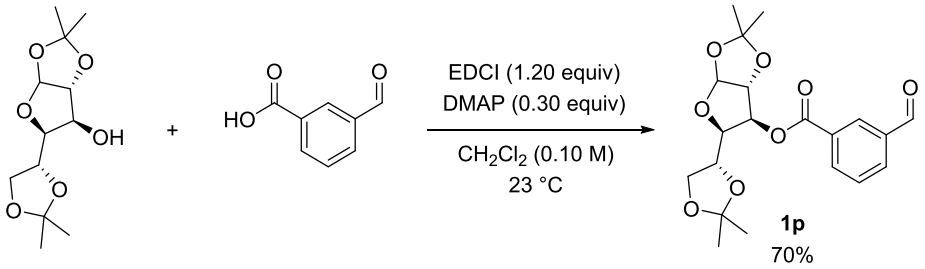



**Figure S2.** A picture of 30W blue LED light.

## Synthesis of Aldehyde Substrates

**(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 3-formylbenzoate (1p)**




*N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (276 mg, 1.44 mmol, 1.20 equiv) was added to a suspension of 3-formylbenzoic acid (180 mg, 1.20 mmol, 1.00 equiv), diacetone-D-glucose (312 mg, 1.20 mmol, 1.00 equiv), and 4-dimethylaminopyridine (44.0 mg, 0.360 mmol, 0.300 equiv) in $CH_2Cl_2$ (12.0 mL, 0.100 M), and the reaction mixture was stirred at 23 °C for 15 h. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (17:3 to 7:3 (v/v)), to afford the title compound as a white solid (327 mg, 0.834 mmol, 70% yield).

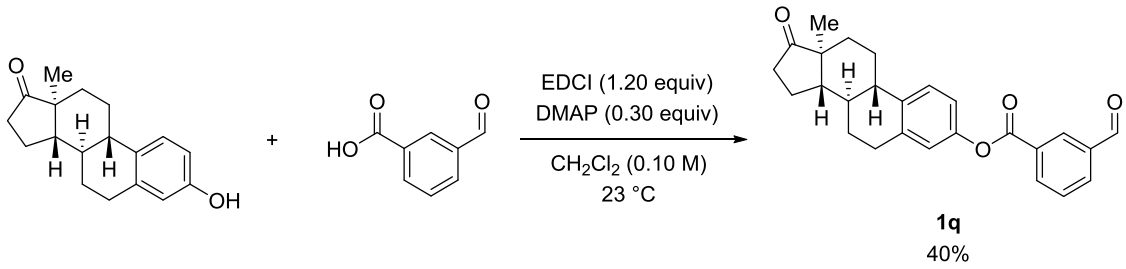
**$R_f$** = 0.59 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 10.07 (s, 1H), 8.48 (t, *J* = 1.8 Hz, 1H), 8.27 (dt, *J* = 7.6, 1.5 Hz, 1H), 8.12–8.08 (m, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 5.96 (d, *J* = 3.7 Hz, 1H), 5.53 (d, *J* = 3.1 Hz, 1H), 4.64 (d, *J* = 3.7 Hz, 1H), 4.37–4.28 (m, 2H), 4.14–4.09 (m, 1H), 4.09–4.05 (m, 1H), 1.54 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H), 1.24 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 191.2, 164.3, 136.8, 135.3, 133.8, 131.2, 130.8, 129.6, 112.5, 109.6, 105.2, 83.5, 80.0, 77.2, 72.6, 67.5, 27.0, 26.8, 26.3, 25.3.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{24}O_8Na$ ($[M + Na]^+$): 415.1363, found: 415.1371.

**(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 3-formylbenzoate (1q)**




*N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (276 mg, 1.44 mmol, 1.20 equiv) was added to a suspension of 3-formylbenzoic acid (180 mg, 1.20 mmol, 1.00 equiv), estrone (324 mg, 1.20 mmol, 1.00 equiv), and 4-dimethylaminopyridine (44.0 mg, 0.360 mmol, 0.300 equiv) in $CH_2Cl_2$

(12.0 mL, 0.100 M), and the reaction mixture was stirred at 23 °C for 15 h. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 1:1 (v/v)), to afford the title compound as a white solid (193 mg, 0.480 mmol, 40% yield).

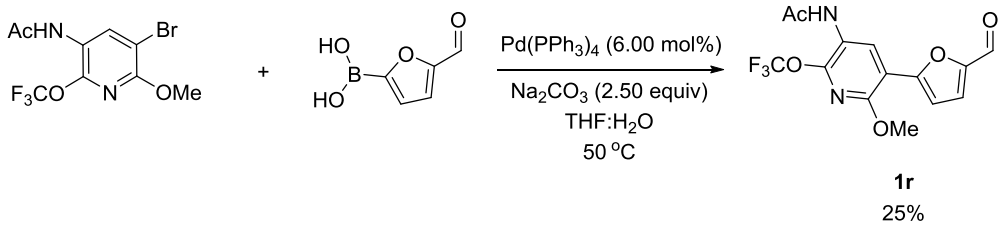
**$R_f$** = 0.53 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 10.13 (s, 1H), 8.69 (s, 1H), 8.45 (d, *J* = 7.8, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.03–6.98 (m, 1H), 6.98–6.95 (m, 1H), 2.98–2.91 (m, 2H), 2.52 (dd, *J* = 19.1, 8.7 Hz, 1H), 2.47–2.40 (m, 1H), 2.38–2.29 (m, 1H), 2.21–2.11 (m, 1H), 2.11–2.02 (m, 2H), 2.01–1.95 (m, 1H), 1.70–1.59 (m, 2H), 1.59–1.43 (m, 4H), 0.93 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 220.9, 191.4, 164.5, 148.7, 138.4, 137.9, 136.8, 135.8, 133.8, 131.8, 130.9, 129.6, 126.7, 121.7, 118.8, 50.6, 48.1, 44.3, 38.1, 36.0, 31.7, 29.6, 26.5, 25.9, 21.7, 14.0.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{26}H_{27}O_4$ ($[M + H]^+$): 403.1904, found: 403.1909.

***N*-(5-(5-Formylfuran-2-yl)-6-methoxy-2-(trifluoromethoxy)pyridin-3-yl)acetamide (1r)**




**1r**
25%

A 20 mL vial was charged with *N*-(5-bromo-6-methoxy-2-(trifluoromethoxy)pyridin-3-yl)acetamide (0.401 g, 1.22 mmol, 1.00 equiv), 5-formylfuran-2-boronic acid (0.234 g, 1.71 mmol, 1.40 equiv), $Pd(PPh_3)_4$ (84.6 mg, 73.2 μmol, 6.00 mol%), and sodium carbonate (0.323 g, 3.05 mmol, 2.50 equiv). THF (3.50 mL) and $H_2O$ (2.61 mL) were added and the suspension was degassed *via* three freeze-pump-thaw cycles. The resulting mixture was stirred at 50 °C for 3 days under nitrogen atmosphere. The reaction mixture was then allowed to cool to 23 °C, $H_2O$ (10 mL) and EtOAc (15 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 1:1 (v/v)) to afford the title compound as an off-white solid (0.104 g, 0.302 mmol, 25% yield).

**$R_f$** = 0.56 (hexanes:EtOAc 1:1 (v/v)).

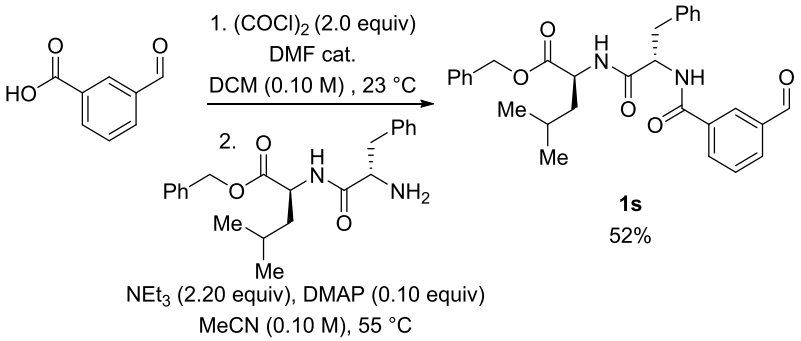
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 9.68 (s, 1H), 8.97 (s, 1H), 7.55 (br. s, 1H), 7.32 (d, *J* = 3.9 Hz, 1H), 7.09 (d, *J* = 3.9 Hz, 1H), 4.00 (s, 3H), 2.29 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 177.8, 168.9, 154.2, 153.3, 151.9, 144.0, 132.4, 123.0, 120.1 (q, *J* = 262.0 Hz), 116.3, 113.0, 110.2, 54.7, 24.3.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –56.4.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{12}F_3N_2O_5$ ($[M + H]^+$): 345.0693, found: 345.0698.

**Benzyl (3-formylbenzoyl)-*L*-phenylalanyl-*L*-leucinate (1s)**




To a suspension of 3-formylbenzoic acid (167 mg, 1.11 mmol, 1.00 equiv) in $CH_2Cl_2$ (11.1 mL, 0.100 M) was added oxalyl chloride (282 mg, 188 µL, 2.22 mmol, 2.00 equiv) and a drop of DMF and the reaction mixture was stirred at 23 °C for 1 h under nitrogen atmosphere. The solvent and the excess of oxalyl chloride were removed *in vacuo.* The residue was dissolved in MeCN (11.1 mL, 0.100 mL). H-Phe-Leu-OBzl (409 mg, 1.11 mmol, 1.00 equiv), DMAP (13.6 mg, 0.111 mmol, 0.100 equiv), and triethylamine (225 mg, 309 µL, 2.22 mmol, 2.00 equiv) were then added and the reaction mixture was stirred at 55 °C for 15 h under nitrogen atmosphere. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 1:1 (v/v)), to afford the title compound as a white solid (287 mg, 0.574 mmol, 52% yield).

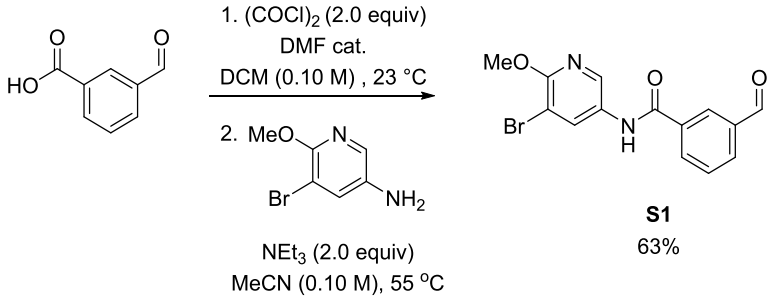
**$R_f$** = 0.36 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 10.00 (s, 1H), 8.20 (t, *J* = 2.0 Hz, 1H), 7.98 (dt, *J* = 7.9, 1.7 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.40–7.29 (m, 6H), 7.25–7.16 (m, 5H), 6.70–6.62 (m, 1H), 5.15 (s, 2H), 5.03–4.94 (m, 1H), 4.65–4.56 (m, 1H), 3.23–3.12 (m, 2H), 1.65–1.58 (m, 1H), 1.57–1.44 (m, 2H), 0.83 (d, *J* = 5.95, 6H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 191.5, 172.2, 171.0, 166.0, 136.6, 136.4, 135.4, 134.8, 132.9, 132.2, 129.5, 129.5, 128.9, 128.8, 128.7, 128.6, 128.4, 127.2, 67.2, 55.0, 51.3, 41.4, 38.6, 24.9, 22.7, 22.0.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{30}H_{33}N_2O_5$ ($[M + H]^+$): 501.2384, found: 501.2388.

***N*-(5-Bromo-6-methoxypyridin-3-yl)-3-formylbenzamide (S1)**




To a suspension of 3-formylbenzoic acid (500 mg, 3.33 mmol, 1.00 equiv) in $CH_2Cl_2$ (33.3 mL, 0.100 M) was added oxalyl chloride (845 mg, 563 µL, 6.66 mmol, 2.00 equiv) and a drop of DMF and the reaction mixture was stirred at 23 °C for 1 h under nitrogen atmosphere. The solvent and the excess of oxalyl

chloride were removed *in vacuo*. The residue was dissolved in MeCN (33.3 mL, 0.100 mL). 5-bromo-6-methoxypyridin-3-amine (676 mg, 3.33 mmol, 1.00 equiv), and triethylamine (674 mg, 928 μL, 6.66 mmol, 2.00 equiv) were then added and the reaction mixture was stirred at 55 °C for 3 h under nitrogen atmosphere. The reaction mixture was then concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 1:1 (v/v)), to afford the title compound as a pink solid (698 mg, 2.08 mmol, 63% yield).

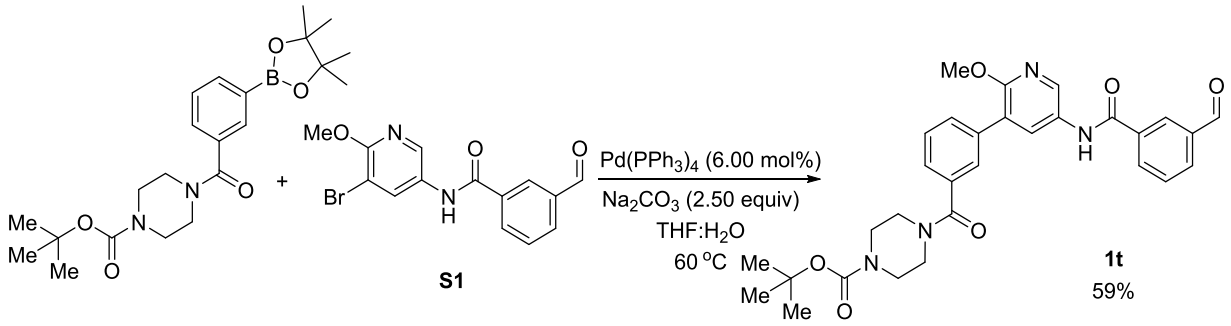
**$R_f$** = 0.24 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $(CD_3)_2SO$, δ): 10.64 (s, 1H), 10.12 (s, 1H), 8.53 (d, *J* = 2.6 Hz, 1H), 8.50 (s, 1H), 8.46 (d, *J* = 2.6 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.80 (t, *J* = 7.6 Hz, 1H), 3.93 (s, 3H).

**$^{13}$C NMR** (176 MHz, $(CD_3)_2SO$, δ): 192.8 (d, *J* = 13.0 Hz), 164.5, 155.8, 137.6, 136.3, 134.9, 134.8, 133.4, 132.8, 130.6, 129.5, 128.3, 105.0, 54.4.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{12}BrN_2O_3$ ($[M + H]^+$): 335.0026, found: 335.0032.

***tert*-Butyl 4-(3-(5-(3-formylbenzamido)-2-methoxypyridin-3-yl)benzoyl)piperazine-1-carboxylate (1t)**




A 20 mL vial was charged with *N*-(5-bromo-6-methoxypyridin-3-yl)-3-formylbenzamide (**S1**) (0.300 g, 0.895 mmol, 1.00 equiv), *tert*-butyl 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)piperazine-1-carboxylate (0.522 g, 1.25 mmol, 1.40 equiv), $Pd(PPh_3)_4$ (62.1 mg, 53.7 μmol, 6.00 mol%), and sodium carbonate (0.237 g, 2.24 mmol, 2.50 equiv). THF (2.56 mL) and $H_2O$ (1.90 mL) were added and the suspension was degassed *via* three freeze-pump-thaw cycles. The resulting mixture was stirred at 60 °C for 15 hours under nitrogen atmosphere. The reaction mixture was then allowed to cool to 23 °C, $H_2O$ (10 mL) and EtOAc (15 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:1 to 0:1 (v/v)), followed by recrystallization from $CH_2Cl_2$:hexanes to afford the title compound as a white solid (0.288 g, 0.530 mmol, 59% yield).

**$R_f$** = 0.75 (EtOAc).

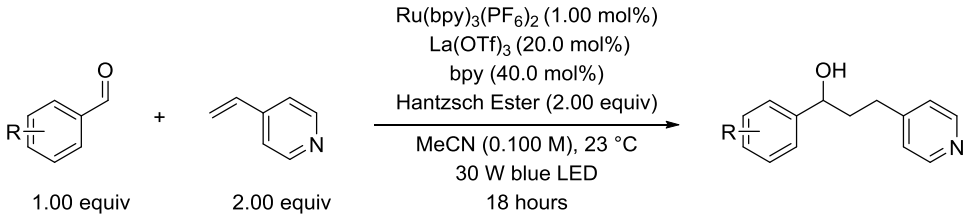
**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 10.06 (s, 1H), 9.03 (s, 1H), 8.45 (s, 1H), 8.38 (d, *J* = 2.4 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.6, 1H), 7.90 (d, *J* = 2.2 Hz, 1 H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 3.92 (s, 3H), 3.79–3.67 (m, 2H), 3.56–3.37 (m, 6H), 1.46 (s, 9H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 191.4, 170.7, 165.0, 158.0, 154.8, 139.0, 136.9, 136.7, 135.6, 135.4, 133.5, 132.9, 132.7, 130.9, 129.7, 129.3, 128.7, 128.1, 128.0, 126.5, 123.3, 80.6, 54.0, 47.8, 44.0, 28.6.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{30}H_{33}N_4O_6$ ($[M + H]^+$): 545.2395, found: 545.2399.

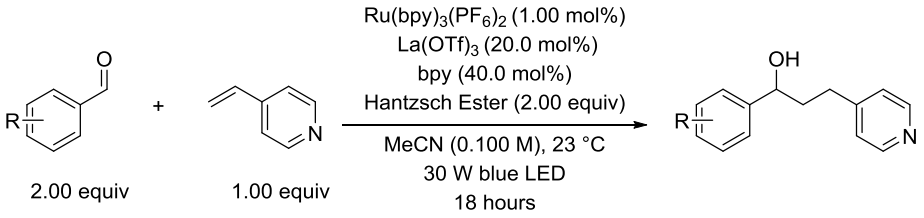
# Coupling of Aldehydes with 4-Vinylpyridine

### General Procedure A (0.5 mmol scale unless otherwise stated)



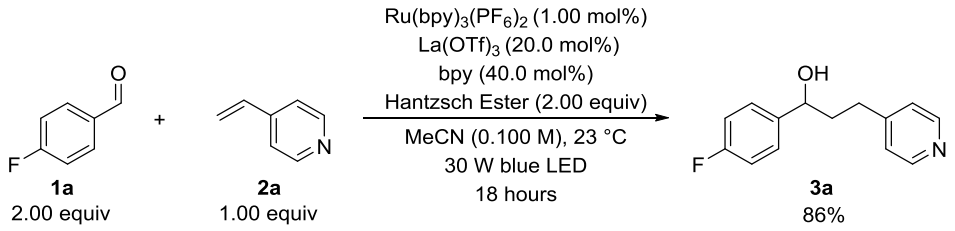

In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (20.0 mol%) and bipyridine (40.0 mol%). MeCN (0.100 M, with respect to aldehyde substrate) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). An aldehyde substrate (1.00 equiv), 4-vinylpyridine (2.00 equiv), Hantzsch Ester (2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (1.00 mol%) were then added. The reaction vial was capped taken out of the glovebox, and placed 30 mm from a blue LED light source (30 W, 455 nm, unless otherwise stated). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc, to afford the desired product.

### General Procedure B (0.5 mmol scale unless otherwise stated)




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (20.0 mol%) and bipyridine (40.0 mol%). MeCN (0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). An aldehyde substrate (2.00 equiv), 4-vinylpyridine (1.00 equiv), Hantzsch Ester (2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (30 W, 455 nm, unless otherwise stated). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc, to afford the desired product.

**1-(4-Fuorophenyl)-3-(pyridin-4-yl)propan-1-ol (3a)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 4-Fluorobenzaldehyde (**1a**) (124 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W ). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the desired product as a white solid (99.4 mg, 0.429 mmol, 86% yield).

$\mathbf{R_f}$ = 0.46 (hexanes:EtOAc 1:4 (v/v)).

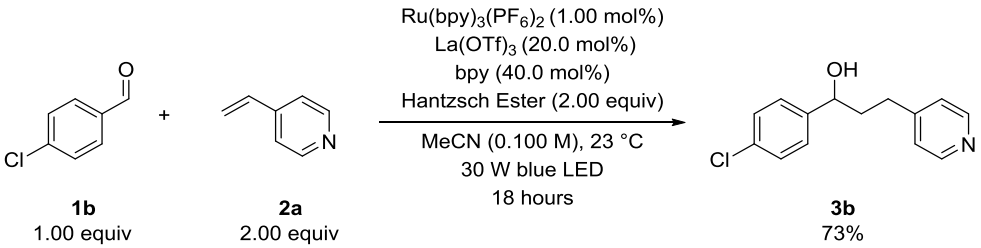
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.1 Hz, 2H), 7.31 (q, *J* = 4.6 Hz, 2H), 7.09 (d, *J* = 5.4 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.66 (t, *J* = 6.4 Hz, 1H), 2.84 (s, 1H), 3.00 (br. s, 1H), 2.73 (m, 1H), 2.66 (m, 1H), 2.10 (m, 1H), 1.97 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 162.36 (d, *J* = 246.6 Hz), 151.02, 149.69, 140.31, 127.60 (d, *J* = 7.6 Hz), 124.05, 115.52 (d, *J* = 21.4 Hz), 72.86, 39.52, 31.44.

**$^{19}$F NMR** (700 MHz, $CDCl_3$) δ -119.85 (m).

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}FNO$ ($[M + H]^+$): 232.1134, found: 232.1134.

**1-(4-Chlorophenyl)-3-(pyridin-4-yl)propan-1-ol (3b)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 4-Chlorobenzaldehyde (**1b**) (70.3 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol,

1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (90.4 mg, 0.365 mmol, 73%).

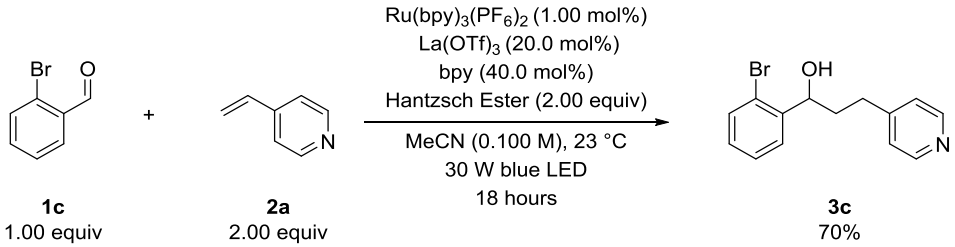
**$R_f$** = 0.40 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.42 (s, 2H), 7.32 (q, *J* = 11.9 Hz, 4H), 7.12 (d, *J* = 4.0 Hz, 2H), 4.68 (t, *J* = 6.1 Hz, 1H), 3.03 (br. s, 1H), 2.73 (m, 2H), 2.05 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.03, 149.63, 143.07, 133.45, 128.81, 127.34, 124.07, 72.75, 39.45, 31.35.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}ClNO$ ($[M + H]^+$): 248.0838, found: 248.0838.

**1-(2-Bromophenyl)-3-(pyridin-4-yl)propan-1-ol (3c)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2-Bromobenzaldehyde (**1c**) (92.5 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (102.3 mg, 0.350 mmol, 70%).

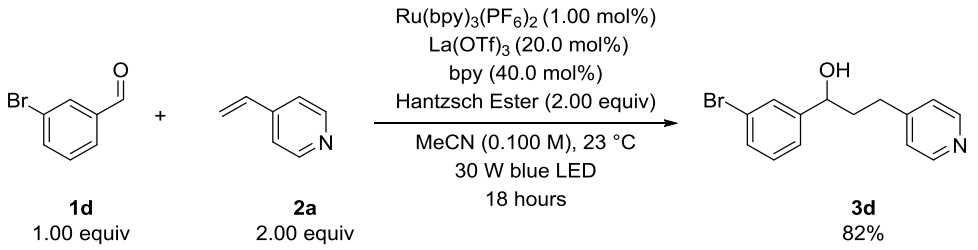
**$R_f$** = 0.45 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 5.5 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 5.04 (dd, *J* = 3.53, 8.65 1H), 4.00 (br. s, 1H), 2.85 (m, 1H), 2.76 (m, 1H), 2.06 (m, 1H), 1.95 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.31, 149.34, 143.88, 132.71, 128.91, 127.85, 127.47, 124.22, 121.83, 71.67, 37.91, 31.52.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}BrNO$ ($[M + H]^+$): 292.0334, found: 292.0334.

**1-(3-Bromophenyl)-3-(pyridin-4-yl)propan-1-ol (3d)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 3-Bromobenzaldehyde (**1d**) (92.5 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (120 mg, 0.410 mmol, 82%).

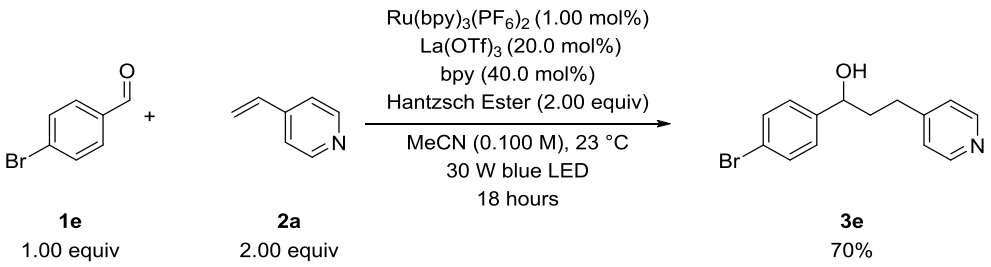
$\mathbf{R}_f$ = 0.35 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.32 (d, *J* = 5.3 Hz, 2H), 7.49 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 5.3 Hz, 2H), 4.62 (dd, *J* = 5.00, 7.80 Hz, 1H), 4.17 (s, 1H), 2.73 (m, 1H), 2.66 (m, 1H), 2.04 (m, 1H), 1.96 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.28, 149.33, 147.23, 130.66, 130.18, 129.06, 124.54, 124.12, 122.72, 72.47, 39.44, 31.33.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}BrNO$ ($[M + H]^+$): 292.0334, found: 292.0334.

**1-(4-Bromophenyl)-3-(pyridin-4-yl)propan-1-ol (3e)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 4-Bromobenzaldehyde (**1e**) (92.5 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol,

1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (102 mg, 0.350 mmol, 70%).

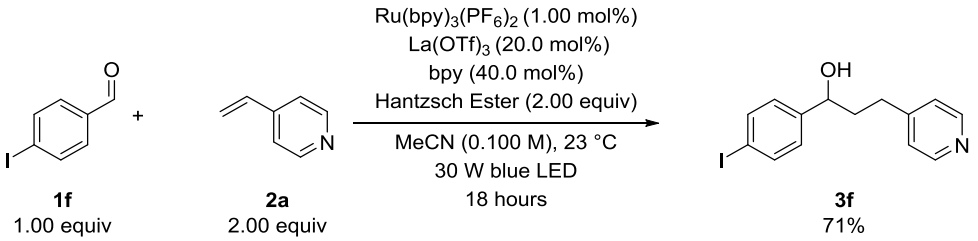
**$R_f$** = 0.32 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.40 (t, *J* = 2.8 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 5.3 Hz, 2H), 4.64 (dd, *J* = 5.21 7.66 Hz 1H), 3.05 (s, 1H), 2.73 (m, 1H), 2.66 (m, 1H), 2.07 (m, 1H), 1.97 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.02, 149.67, 143.63, 131.78, 127.72, 124.09, 121.58, 72.80, 39.44, 31.36.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}BrNO$ ($[M + H]^+$): 292.0334, found: 292.0334.

**1-(4-Iodophenyl)-3-(pyridin-4-yl)propan-1-ol (3f)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 4-Iodobenzaldehyde (**1f**) (116 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (120 mg, 0.355 mmol, 71%).

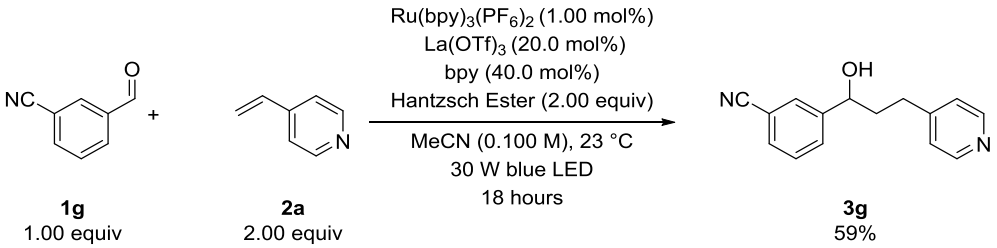
**$R_f$** = 0.32 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.46 (d, *J* = 5.5 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 4H), 4.64 (dd, *J* = 5.18 7.77 Hz, 1H), 2.74 (m, 1H), 2.67 (m, 1H), 2.08 (m, 1H), 1.97 (m, 1H), 1.76 (s, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 150.74, 149.66, 143.96, 137.68, 127.81, 123.93, 93.14, 72.92, 39.22, 31.2.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{15}INO$ ($[M + H]^+$): 340.0195, found: 340.0195.

**3-(1-Hydroxy-3-(pyridin-4-yl)propyl)benzonitrile (3g)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 3-Formylbenzonitrile (**1g**) (65.6 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (70.3 mg, 0.295 mmol, 59%).

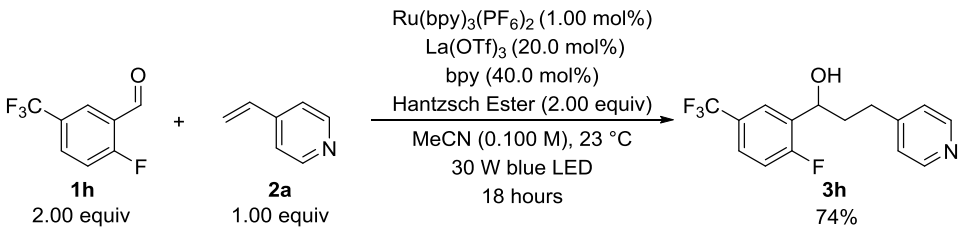
$R_f$ = 0.21 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.1 Hz, 2H), 7.66 (s, 1H), 7.57 (t, *J* = 8.6 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 5.4 Hz, 2H), 4.74 (dd, *J* = 4.59, 8.16 Hz, 1H), 2.94 (br. s, 1H), 2.77 (m, 1H), 2.72 (m, 1H), 2.07 (m, 1H), 2.01 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 150.78, 149.67, 146.16, 131.44, 130.36, 129.59, 129.50, 124.10, 118.85, 112.73, 72.40, 39.55, 31.26.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{15}N_2O$ ($[M + H]^+$): 239.1181, found: 239.1181.

**1-(2-Fluoro-5-(trifluoromethyl)phenyl)-3-(pyridin-4-yl)propan-1-ol (3h)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2-Fluoro-5-(trifluoromethyl)benzaldehyde (**1h**) (192 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken

out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the desired product as a white solid (111 mg, 0.370 mmol, 74% yield).

**$R_f$** = 0.56 (hexanes:EtOAc 1:4 (v/v)).

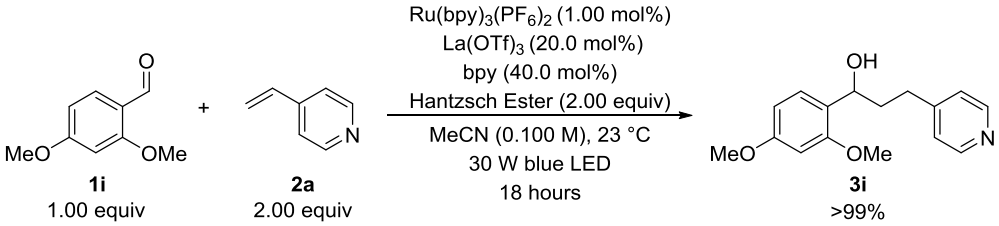
$^1$H NMR (700 MHz, $CDCl_3$) δ 8.37 (d, *J* = 5.0 Hz, 2H), 7.86 (d, *J* = 6.0 Hz, 1H), 7.51 (t, *J* = 3.3 Hz, 1H), 7.10 (q, *J* = 8.7 Hz, 3H), 5.06 (t, *J* = 6.3 Hz, 1H), 3.91 (br. s, 1H), 2.83 (m, 1H), 2.75 (m,1H), 2.07 (q, *J* = 7.4 Hz, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 161.27 (d, *J* = 250.0 Hz), 151.05, 149.40, 133.05 (d, *J* = 14.1 Hz), 127.13 (qd, *J* = 3.58 Hz, *J* = 32.3 Hz), 126.35 (m), 125.14 (t), 124.16, 123.91 (q, *J* = 271.7 Hz), 115.97 (d, *J* = 23.6 Hz), 66.55, 38.23, 31.24.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.52, -114.75.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{14}F_4NO$ ($[M + H]^+$): 300.1008, found: 300.1008.

**1-(2,4-Dimethoxyphenyl)-3-(pyridin-4-yl)propan-1-ol (3i)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Dimethoxybenzaldehyde (**1i**) (83.1 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a colorless liquid (136 mg, 0.498 mmol, >99% yield).

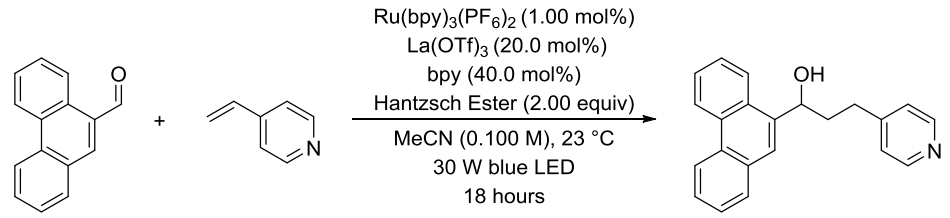
**$R_f$** = 0.23 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 5.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 5.5 Hz, 2H), 6.43 (q, *J* = 3.4 Hz, 1H), 6.39 (d, *J* = 1.9 Hz, 1H), 4.84 (dd, *J* = 5.11, 7.70 Hz, 2H), 3.90 (br. s, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.75 (m, 1H), 2.63 (m, 1H), 2.02 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 160.00, 157.33, 151.69, 149.25, 127.32, 125.08, 124.01, 104.12, 98.45, 68.46, 55.30, 55.20, 37.68, 31.58.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{16}H_{20}NO_3$ ($[M + H]^+$): 274.1442, found: 274.1442.

**1-(Phenanthren-9-yl)-3-(pyridin-4-yl)propan-1-ol (3j)**




**1j** 2.00 equiv + **2a** 1.00 equiv → **3j** >99%

In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). Phenanthrene-9-carbaldehyde (**1j**) (206 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the desired product as a white solid (157 mg, 0.500 mmol, >99% yield).

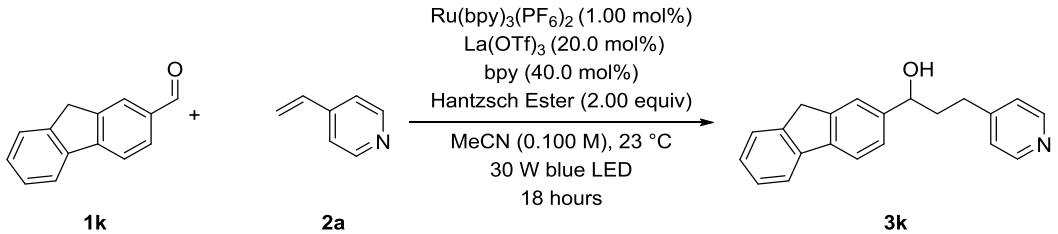
**$R_f$ =** 0.31 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.48 (d, *J* = 5.7 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.94 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.66 (m, *J* = 6.2 Hz, 2H), 7.60 (q, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 5.7 Hz, 2H), 5.49 (dd, *J* = 8.09, 3.74 Hz, 1H), 2.90 (m, 2H), 2.30 (m, *J* = 4.8 Hz, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.12, 149.77, 138.10, 131.44, 130.95, 130.20, 129.49, 128.88, 127.02, 126.94, 126.84, 126.57, 124.19, 123.87, 123.64, 123.61, 122.62, 70.42, 38.17, 31.75.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{22}H_{20}NO$ ($[M + H]^+$): 314.1542, found: 314.1542.

**1-(9*H*-Fluoren-2-yl)-3-(pyridin-4-yl)propan-1-ol (3k)**




**1k** 1.00 equiv + **2a** 2.00 equiv → **3k** 84%

In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 9*H*-Fluorene-2-carbaldehyde (**1k**) (97.1 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (126 mg, 0.420 mmol, 84%).

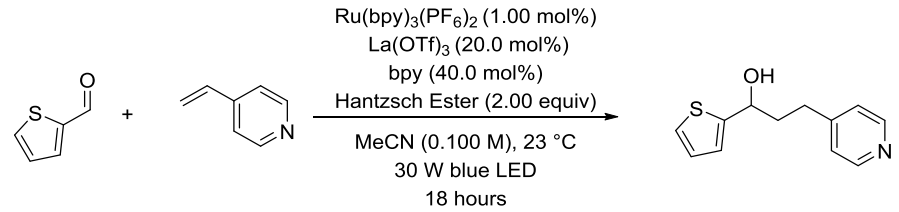
$\mathbf{R}_f$ = 0.21 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.5 Hz, 2H), 7.77 (q, *J* = 7.0 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 5.7 Hz, 2H), 4.76 (dd, *J* = 4.75, 7.70 Hz, 1H), 3.90 (s, 1H), 2.78 (m,1H), 2.70 (m, 1H), 2.19 (m, 1H), 2.07 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.15, 149.77, 143.87, 143.48, 143.02, 141.69, 141.41, 126.96, 125.22, 124.81, 124.11, 122.66, 120.05 (d, *J* = 2.4 Hz), 73.97, 39.50, 37.03, 31.60.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{21}H_{20}NO$ ($[M + H]^+$): 302.1544, found: 302.1544.

**3-(Pyridin-4-yl)-1-(thiophen-2-yl)propan-1-ol (3l)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). Thiophene-2-carbaldehyde (**1l**) (56.1 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a colorless liquid (80.0 mg, 0.365 mmol, 73%).

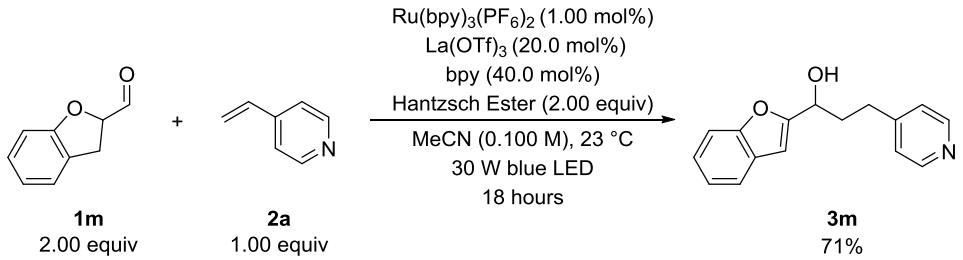
$\mathbf{R}_f$ = 0.13 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.7 Hz, 2H), 7.32 (q, *J* = 2.6 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.12 (d, *J* = 5.3 Hz, 2H), 7.08 (d, *J* = 5.0 Hz, 1H), 4.79 (dd, *J* = 5.42, 7.59 Hz, 1H), 2.76 (m, 1H), 2.69 (m, 1H), 2.34 (br. s, 1H), 2.14 (m, 1H), 2.07 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 151.18, 149.67, 145.89, 126.65, 125.60, 124.13, 121.16, 69.67, 38.72, 31.40.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{12}H_{14}NOS$ ($[M + H]^+$): 220.0792, found: 220.0792.

**1-(Benzofuran-2-yl)-3-(pyridin-4-yl)propan-1-ol (3m)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,3-Dihydrobenzofuran-2-carbaldehyde (**1m**) (148.2 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the desired product as an off white solid (89.9 mg, 0.355 mmol, 71% yield).

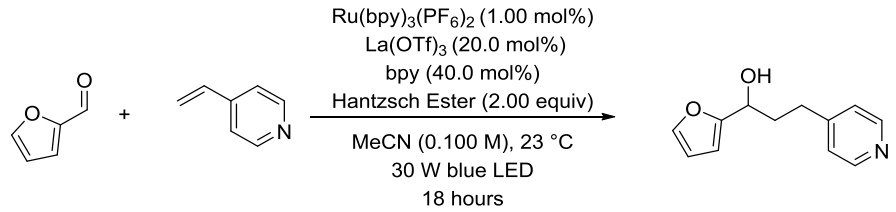
**$R_f$** = 0.32 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.4 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.25 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 5.5 Hz, 2H), 6.62 (s, 1H), 4.81 (t, *J* = 6.6 Hz, 1H), 3.49 (br. s, 1H), 2.77 (m, 2H), 2.24 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 159.27, 154.87, 150.97, 149.56, 128.16, 124.36, 124.17, 122.98, 121.17, 111.34, 102.88, 67.14, 35.99, 31.04.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{16}H_{16}NO_2$ ($[M + H]^+$): 254.1180, found: 254.1180.

**1-(Furan-2-yl)-3-(pyridin-4-yl)propan-1-ol (3n)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). Furan-2-carbaldehyde (**1n**) (48.1 mg, 0.500 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (105 mg, 1.00 mmol, 2.00 equiv., Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (69.1 mg, 0.340 mmol, 68%).

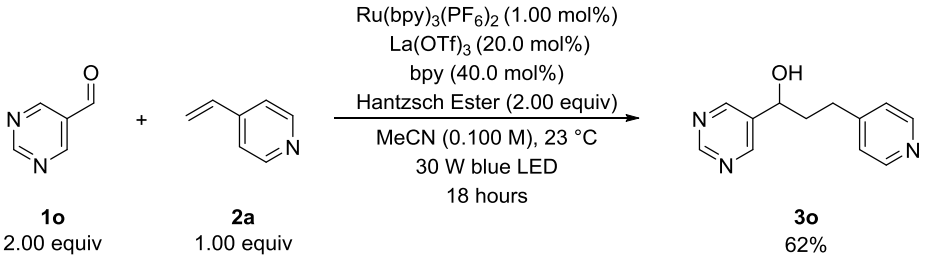
$\mathbf{R_f}$ = 0.14 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.36 (d, *J* = 5.0 Hz, 2H), 7.33 (d, *J* = 0.8 Hz, 1H), 7.10 (d, *J* = 5.5 Hz, 2H), 6.30 (q, *J* = 1.6 Hz, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 4.65 (t, *J* = 6.7 Hz, 1H), 3.76 (br. s, 1H), 2.75 (m, 1H), 2.67 (m, 1H), 2.14 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 156.74, 151.31, 149.23, 141.92, 124.13, 110.21, 105.98, 66.39, 35.97, 31.12.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{12}H_{14}NO_2$ ($[M + H]^+$): 204.1020, found: 204.1020.

**3-(Pyridin-4-yl)-1-(pyrimidin-5-yl)propan-1-ol (3o)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). Pyrimidine-5-carbaldehyde (**1o**) (108.1 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$

(4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with EtOAc:MeOH:TEA (80:10:1 (v/v/v)) to afford the desired product as an off-white solid (66.7 mg, 0.310 mmol, 62% yield).

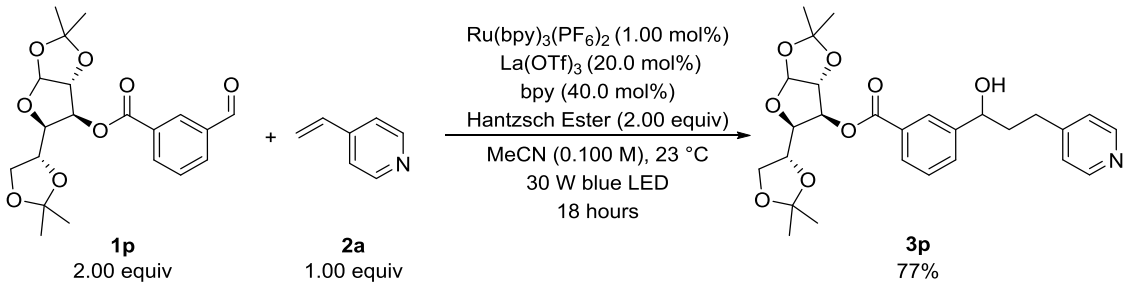
**$R_f$** = 0.33 (EtOAc:MeOH:TEA 80:10:1 (v/v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.70 (s, 2H), 8.35 (d, *J* = 5.6 Hz, 2H), 7.11 (d, *J* = 5.6 Hz, 2H), 4.74 (dd, *J* = 8.47, 4.48 Hz, 1H), 2.78 (m, 2H), 2.12 (m, 1H), 2.02 (m, 1H).

**$^{13}$C NMR (**176 MHz, $CDCl_3$) δ 157.92, 154.94, 150.82, 149.38, 137.81, 124.18, 68.76, 39.23, 31.12.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{12}H_{14}N_3O$ ($[M + H]^+$): 216.1132, found: 216.1132.

**(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 3-(1-hydroxy-3-(pyridin-4-yl)propyl)benzoate (3p)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (11.7 mg, 20.0 μmol, 20.0 mol%) and bipyridine (6.24 mg, 40.0 μmol, 40.0 mol%). MeCN (1.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (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 3-formylbenzoatecarbamate (**1p**) (78.48 mg, 0.200 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (10.5 mg, 0.100 mmol, 1.00 equiv.), Hantzsch Ester (50.7 mg, 0.200 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (0.860 mg, 1.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by preparative TLC, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a white solid (38.5 mg, 0.077 mmol, 77%).

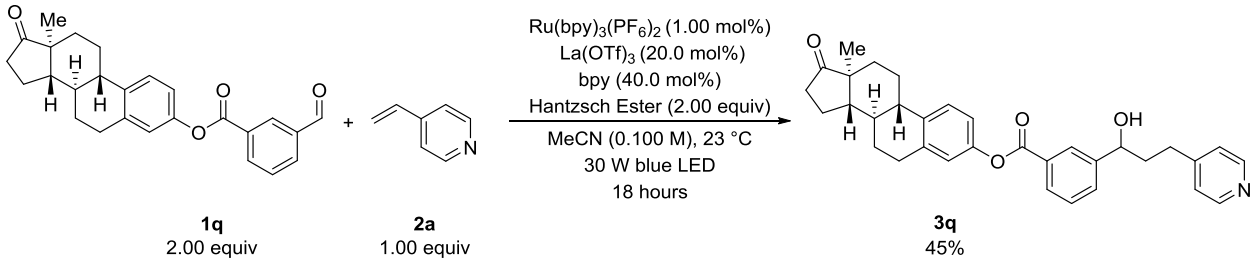
$R_f$ = 0.28 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.49 (d, *J* = 4.8 Hz, 2H), 8.00 (d, *J* = 1.5 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 5.5 Hz, 2H), 5.96 (t, *J* = 1.8 Hz, 1H), 5.51 (d, *J* = 2.5 Hz, 1H), 4.78 (q, *J* = 4.2 Hz, 1H), 4.63 (t, *J* = 2.9 Hz, 1H), 4.34 (m, 2H), 4.10 (m, 2H), 2.79 (q, 1H), 2.72 (m, 1H), 2.12 (m, 2H), 2.03 (m, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.26 (d, *J* = 1.8 Hz, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 165.19, 149.38, 145.08, 131.01, 130.95, 130.00, 129.22, 129.17, 129.07, 129.06, 127.23, 127.22, 124.17, 112.54, 109.54, 105.25, 83.50, 80.04, 73.14, 73.10, 72.71, 67.39, 39.47, 31.72, 31.43 (d, *J* = 3.9 Hz), 26.96, 26.85, 26.34, 25.37.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{27}H_{34}NO_8$ ($[M + H]^+$): 500.2288, found: 500.2288.

**(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 3-(3-(pyridin-4-yl)propanoyl)benzoate (3q)**




**1q** 2.00 equiv | **2a** 1.00 equiv | **3q** 45%

In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (11.7 mg, 20.0 μmol, 20.0 mol%) and bipyridine (6.24 mg, 40.0 μmol, 40.0 mol%). MeCN (1.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (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 3-formylbenzoate (**1q**) (80.4 mg, 0.200 mmol, 2.00 equiv), 4-vinylpyridine (**2a**) (10.5 mg, 0.100 mmol, 1.00 equiv.), Hantzsch Ester (50.7 mg, 0.200 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (0.860 mg, 1.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by preparative TLC, eluting with EtOAc:MeOH (20:1 (v/v)) to afford the title compound as a white solid (22.8 mg, 0.045 mmol, 45%).

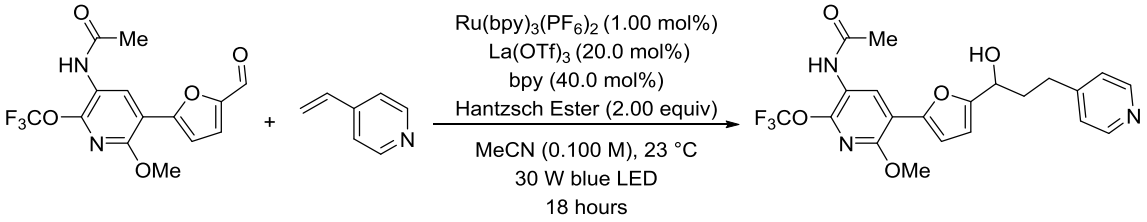
**$R_f$** = 0.33 (EtOAc:MeOH 20:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.16 (s, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 4.8 Hz, 2H), 6.98 (q, *J* = 3.5 Hz, 1H), 6.94 (s, 1H), 4.80 (dd, *J* = 4.9, 8.0 Hz, 1H), 2.94 (q, *J* = 5.1 Hz, 2H), 2.81 (m, *J* = 4.9 Hz, 1H), 2.73 (m, *J* = 5.1 Hz, 1H), 2.52 (q, *J* = 9.3 Hz, 1H), 2.43 (q, *J* = 5.4 Hz, 1H), 2.32 (d, *J* = 10.8 Hz, 1H), 2.16 (m, *J* = 9.2 Hz, 2H), 2.05 (m, *J* = 4.8 Hz, 3H), 1.98 (d, *J* = 12.7 Hz, 1H), 1.57 (m, *J* = 6.3 Hz, 7H), 0.93 (s, 3H)

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 165.41, 151.06, 149.65, 148.88, 145.07, 138.29, 137.70, 131.07, 130.14, 129.72, 129.09, 127.61, 126.67, 124.17, 121.79, 118.95, 73.20, 50.58, 48.11, 44.32, 39.49, 38.14, 36.01, 31.73, 31.69, 31.45, 29.59, 26.49, 25.92, 22.80, 21.74, 14.27, 13.98.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{33}H_{36}NO_4$ ($[M + H]^+$): 510.2642, found: 510.2642.

**_N_-(5-(5-(1-Hydroxy-3-(pyridin-4-yl)propyl)furan-2-yl)-6-methoxy-2-(trifluoromethoxy)pyridin-3-yl)acetamide (3r)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (11.7 mg, 20.0 μmol, 20.0 mol%) and bipyridine (6.24 mg, 40.0 μmol, 40.0 mol%). MeCN (1.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). *N*-(5-(5-Formylfuran-2-yl)-6-methoxy-2-(trifluoromethoxy)pyridin-3-yl)acetamide (**1r**) (34.4 mg, 0.100 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (21.0 mg, 0.200 mmol, 2.00 equiv.), Hantzsch Ester (50.7 mg, 0.200 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (0.860 mg, 1.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by preparative TLC, eluting with EtOAc:MeOH (100:1 (v/v)) to afford the title compound as a white solid (20.4 mg, 0.045 mmol, 45%).

**$R_f$** = 0.30 (EtOAc:MeOH 100:1 (v/v)).

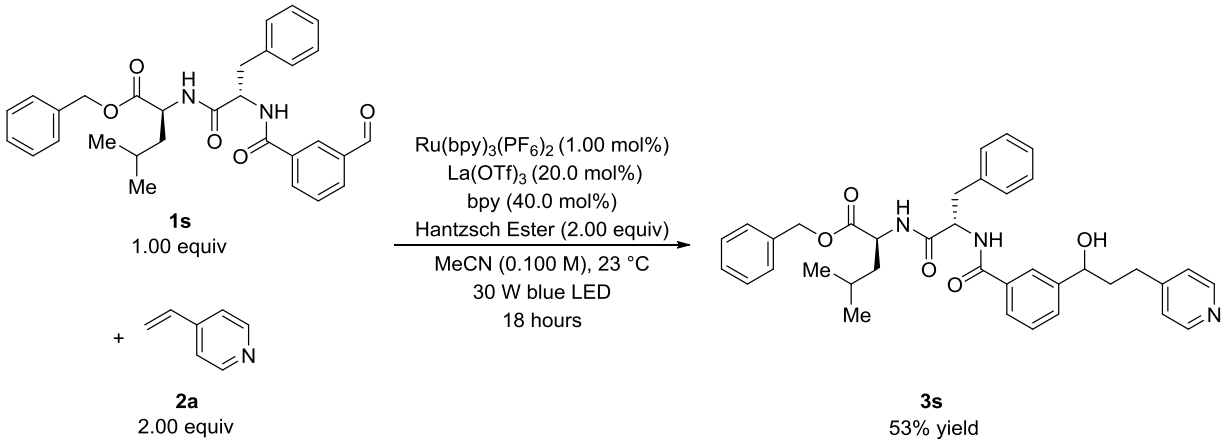
**$^1$H NMR** (700 MHz, MeOD) δ 8.49 (s, 1H), 8.40 (d, *J* = 5.9 Hz, 2H), 7.32 (d, *J* = 6.0 Hz, 2H), 6.93 (d, *J* = 3.4 Hz, 1H), 6.43 (d, *J* = 3.2 Hz, 1H), 4.70 (t, *J* = 6.7 Hz, 1H), 4.04 (s, 3H), 2.86 (m, 1H), 2.77 (m, 1H), 2.23 (m, 2H), 2.20 (s, 3H).

**$^{13}$C NMR** (176 MHz, MeOD) δ 172.60, 158.36, 155.36, 154.01, 150.01, 148.02, 145.75, 134.38, 125.90, 121.79 (q, *J* = 260.2 Hz, 1C), 117.12, 113.72, 112.81, 109.70, 67.61, 54.96, 37.35, 32.29, 23.22.

**$^{19}$F NMR** (376 MHz, MeOD) δ -56.38.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{21}H_{21}F_3N_3O_5$ ($[M + H]^+$): 452.1432, found: 452.1432.

**Benzyl (3-(1-hydroxy-3-(pyridin-4-yl)propyl)benzoyl)-*L*-phenylalanyl-*L*-leucinate (3s)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (11.7 mg, 20.0 μmol, 20.0 mol%) and bipyridine (6.24 mg, 40.0 μmol, 40.0 mol%). MeCN (1.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). Benzyl (3-formylbenzoyl)-*L*-phenylalanyl-*L*-leucinate (**1s**) (50.1 mg, 0.100 mmol, 1.00 equiv), 4-vinylpyridine (**2a**) (21.0 mg, 0.200 mmol, 2.00 equiv.), Hantzsch Ester (50.7 mg, 0.200 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (0.860 mg, 1.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by preparative TLC, eluting with EtOAc:MeOH:TEA (100:1:1 (v/v/v)) to afford the title compound as a white solid (32.2 mg, 0.053 mmol, 53%).

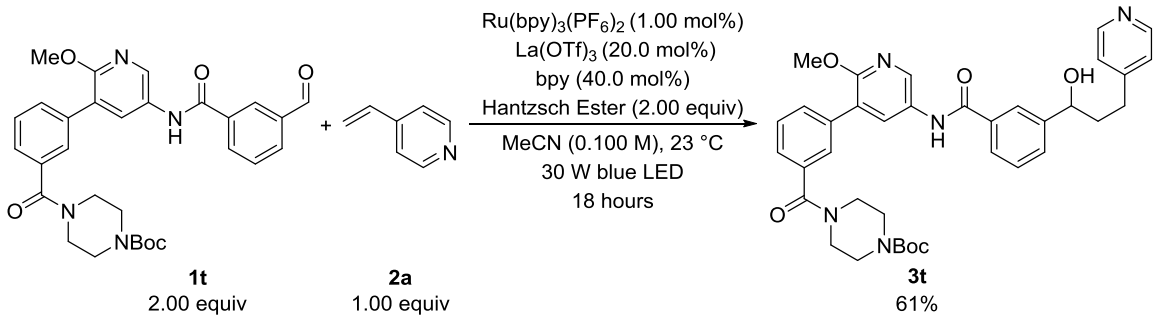
**$R_f$** = 0.27 (EtOAc:MeOH:TEA 100:1:1 (v/v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.47 (br. s, 2H), 7.72 (d, *J* = 2.1 Hz, 1H), 7.58 (t, *J* = 6.5 Hz, 1H), 7.47 (dd, *J* = 12.67 Hz, *J* = 11.50 Hz, 1H), 7.36 (m, 6H), 7.24 (m, 4H), 7.21 (q, *J* = 3.7 Hz, 1H), 7.12 (br. s, 2H), 7.01 (dd, *J* = 7.48 Hz, *J* = 28.49, 1H), 6.39 (q, *J* = 7.8 Hz, 1H), 5.14 (m, 2H), 4.89 (q, *J* = 7.0 Hz, 1H), 4.71 (t, *J* = 6.4 Hz, 1H), 4.57 (q, *J* = 7.3 Hz, 1H), 3.20 (dd, *J* = 6.7 Hz, 1H), 3.12 (dd, *J* = 7.1 Hz, 1H), 2.77 (m, 1H), 2.68 (m, 1H), 2.08 (m, 1H), 1.99 (m, 1H), 1.59 (m, 1H), 1.49 (m, 3H), 0.83 (d, *J* = 6.4 Hz, 6H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 172.29, 170.87, 170.82, 167.12, 149.41 (d, *J* = 9.2 Hz, 1C), 145.22 (d, *J* = 6.1 Hz, 1C), 136.56, 136.54, 135.41, 134.18, 134.15, 129.57, 129.42, 129.36, 129.04, 128.99, 128.82, 128.78, 128.64, 128.41, 127.24, 126.35, 124.85, 124.77, 124.22, 73.15, 67.27, 54.85, 51.31, 41.42, 39.40, 39.36, 38.56, 38.55, 31.48, 31.45, 29.84, 24.90, 22.77, 22.05.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{37}H_{42}N_3O_5$ ($[M + H]^+$): 608.3122, found: 608.3122.

***tert*-Butyl 4-(3-(5-(3-(1-hydroxy-3-(pyridin-4-yl)propyl)benzamido)-2-methoxypyridin-3-yl)benzoyl)piperazine-1-carboxylate (3t)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (11.7 mg, 20.0 μmol, 20.0 mol%) and bipyridine (6.24 mg, 40.0 μmol, 40.0 mol%). MeCN (1.00 mL, 0.100 M, with respect to the aldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). *tert*-Butyl 4-(3-(5-(3-formylbenzamido)-2-methoxypyridin-3-yl)benzoyl)piperazine-1-carboxylate (**1t**) (109 mg, 0.200 mmol, 2.00 equiv.), 4-vinylpyridine (**2a**) (10.5 mg, 0.200 mmol, 2.00 equiv), Hantzsch Ester (50.7 mg, 0.200 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (0.860 mg, 1.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel, eluting with EtOAc:MeOH:TEA (100:1:1 (v/v/v)) to afford the title compound as a white solid (34.5 mg, 0.0610 mmol, 61%).

$\mathbf{R_f}$ = 0.46 EtOAc:MeOH:TEA (100:1:1 (v/v/v)).

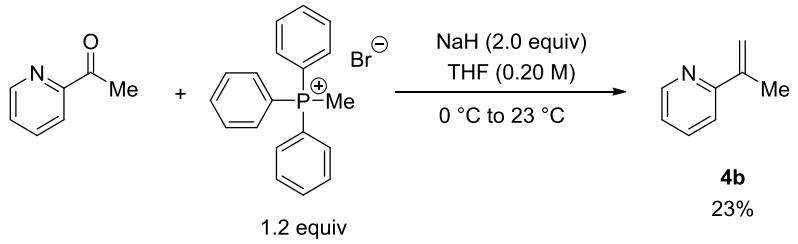
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.36 (d, *J* = 18.3 Hz, 3H), 7.90 (d, *J* = 15.8 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.39 (m, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 4.2 Hz, 2H), 4.67 (dd, *J* = 4.9, 7.9 Hz, 1H), 3.92 (s, 3H), 3.72 (br. s, 2H), 3.44 (br. t, *J* = 37.9 Hz, 6H), 2.74 (m, 1H), 2.66 (m, 1H), 2.06 (m, 1H), 1.97 (m, 1H), 1.46 (s, 9H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 170.65, 166.32, 157.68, 154.71, 151.68, 149.20, 145.50, 138.69, 136.64, 135.20, 134.48, 132.66, 130.93, 129.57, 129.49, 128.99, 128.73, 127.94, 126.67, 126.42, 124.86, 124.29, 123.19, 80.62, 72.85, 54.00, 39.43, 31.45, 28.50.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{37}H_{42}N_5O_6$ ($[M + H]^+$): 652.3130, found: 652.3130.

# Synthesis of 2-Vinylpyridine Substrates

### 2-(Prop-1-en-2-yl)pyridine (4b)



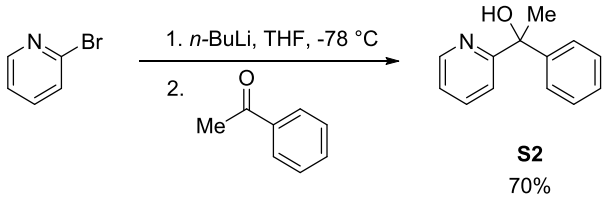

A suspension of methyltriphenylphosphonium bromide (4.61 g, 12.9 mmol, 1.20 equiv) in THF (53.8 mL, 0.200 M) was cooled to 0 °C. NaH (60% dispersion in mineral oil) (0.860 mg, 21.5 mmol, 1.20 equiv) was added and the reaction mixture was stirred at 0 °C for 5 min. 2-Acetylpyridine (1.30 g, 1.21 mL, 10.8 mmol, 1.00 equiv) was then added and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$ (aq) (50.0 mL) and EtOAc (30.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 30.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford the title compound as a clear oil (0.290 g, 2.43 mmol, 23% yield).

$\mathbf{R}_f$ = 0.64 (hexanes:EtOAc 4:1 (v/v)).

**$^1$H NMR** (300 MHz, $CDCl_3$, δ): 8.58 (d, *J* = 4.1 Hz, 1H), 7.64 (m, *J* = 3.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.15 (m, *J* = 3.1 Hz, 1H), 5.85 (s, 1H), 5.30 (d, *J* = 1.3 Hz, 1H), 2.21 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$, δ): 158.4, 149.0, 143.3, 136.4, 122.2, 119.9, 115.8, 20.6.

### 1-Phenyl-1-(pyridin-2-yl)ethan-1-ol (S2)



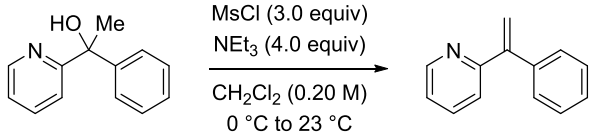

A solution of 2-bromopyridine (2.37 g, 1.43 mL, 15.0 mmol, 1.00 equiv) in THF (18.8 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (15.8 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, acetophenone (1.80 g, 1.75 mL, 15.0 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 4:2 (v/v)), to afford the title compound as a light brown oil (2.09 g, 10.5 mmol, 70% yield).

$\mathbf{R}_f$ = 0.48 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$), δ): 8.53 (dd, *J* = 4.3, 0.9 Hz, 1H), 7.65 (td, *J* = 7.7, 1.7 Hz, 1H), 7.50–7.47 (m, 2H), 7.33–7.28 (m, 3H), 7.25–7.21 (m, 1H), 7.18 (dd, *J* = 7.5, 4.5 Hz, 1H), 5.85 (s, 1H), 1.93 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 164.9, 147.5, 147.2, 137.1, 128.3, 127.1, 126.0, 122.2, 120.4, 75.2, 29.3.

**2-(1-Phenylvinyl)pyridine (4c)**




**S2** **4c** 38%

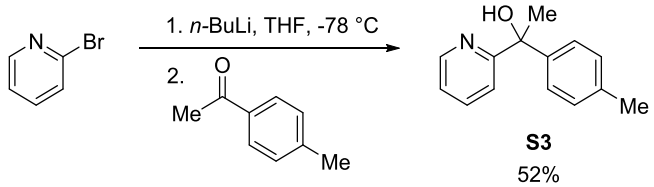
A solution of 1-phenyl-1-(pyridin-2-yl)ethan-1-ol (**S2**) (1.00 g, 5.02 mmol, 1.00 equiv) in $CH_2Cl_2$ (25.1 mL, 0.200 M) was cooled to 0 °C. Triethylamine (2.03 g, 2.80 mL, 22.1 mmol, 4.00 equiv) and methanesulfonyl chloride (1.73 g, 1.17 mL, 15.1 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 17:3 (v/v)), to afford the title compound as a yellow oil (0.342 g, 1.89 mmol, 38% yield).

$\mathbf{R}_f$ = 0.65 (hexanes:EtOAc 4:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.65 (dd, *J* = 4.7, 1.7 Hz, 1H), 7.63 (td, *J* = 7.7, 1.7 Hz, 1H), 7.38–7.32 (m, 5H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.21 (dd, *J* = 7.5, 4.5 Hz, 1H), 6.01 (d, *J* = 1.1 Hz, 1H), 5.61 (d, *J* = 1.1 Hz, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 158.6, 149.5, 149.3, 140.5, 136.4, 128.5, 128.4, 128.0, 123.0, 122.6, 117.9.

**1-(Pyridin-2-yl)-1-(*p*-tolyl)ethan-1-ol (S3)**




**S3** 52%

A solution of 2-bromopyridine (3.16 g, 1.91 mL, 20.0 mmol, 1.00 equiv) in THF (25.0 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (21.0 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 4'-methylacetophenone (2.68 g, 2.67 mL, 20.0 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel,

eluting with hexanes:EtOAc (9:1 to 4:1 (v/v)), to afford the title compound as a white solid (2.23 g, 10.5 mmol, 52% yield).

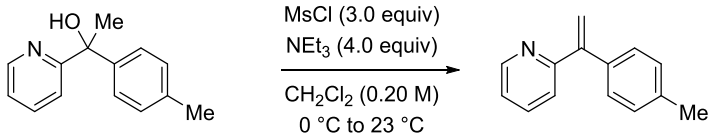
**$R_f$** = 0.52 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.52 (d, *J* = 4.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.81 (br. s, 1H), 2.31 (s, 3H), 1.92 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 165.1, 147.4, 144.3, 137.1, 136.7, 129.0, 125.9, 122.1, 120.4, 75.0, 29.3, 21.1.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{16}NO$ ($[M + H]^+$): 214.1226, found: 214.1230.

**2-(1-(*p*-Tolyl)vinyl)pyridine (4d)**




**S3** **4d** 65%

A solution of 1-(pyridin-2-yl)-1-(*p*-tolyl)ethan-1-ol (**S3**) (1.70 g, 7.97 mmol, 1.00 equiv) in $CH_2Cl_2$ (40.0 mL, 0.200 M) was cooled to 0 °C. Triethylamine (3.23 g, 4.44 mL, 31.9 mmol, 4.00 equiv) and methanesulfonyl chloride (2.74 g, 1.85 mL, 23.9 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford the title compound as a yellow oil (1.01g, 5.17 mmol, 65% yield).

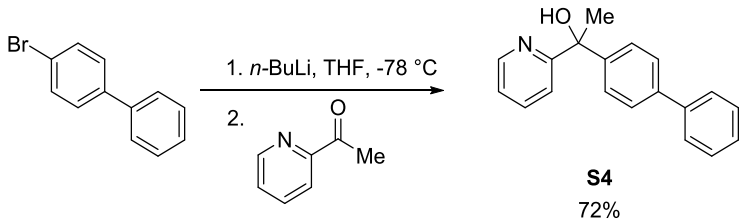
**$R_f$** = 0.64 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.65 (d, *J* = 4.7 Hz, 1H), 7.63 (td, *J* = 7.7, 2.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.21 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.95 (s, 1H), 5.60 (s, 1H), 2.38 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 158.8, 149.4, 149.1, 137.7, 137.6, 136.2, 129.1, 128.4, 122.9, 122.5, 117.2, 21.3.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{14}H_{14}N$ ($[M + H]^+$): 196.1121, found: 196.1122.

**1-([1,1'-Biphenyl]-4-yl)-1-(pyridin-2-yl)ethan-1-ol (S4)**




A solution of 4-bromobiphenyl (3.50 g, 15.0 mmol, 1.00 equiv) in THF (18.8 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (15.8 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 2-acetylpyridine (1.82 g, 1.68 mL, 15.0 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 7:3 (v/v)), to afford the title compound as a white solid (2.98 g, 10.8 mmol, 72% yield).

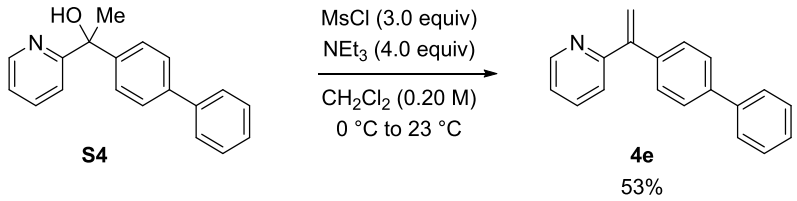
$\mathbf{R_f}$ = 0.44 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.55 (dd, *J* = 4.3, 0.9 Hz, 1H), 7.68 (td, *J* = 7.6, 1.9 Hz, 1H), 7.60–7.54 (m, 6H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.35–7.32 (m, 1H), 7.20 (dd, *J* = 7.5, 4.5 Hz, 1H), 5.89 (br s, 1H), 1.98 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 164.8, 147.6, 146.4, 140.9, 140.0, 137.2, 128.8, 127.3, 127.2, 127.1, 126.5, 122.2, 120.4, 75.1, 29.4.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{19}H_{18}NO$ ($[M + H]^+$): 276.1383, found: 276.1384.

**2-(1-([1,1'-Biphenyl]-4-yl)vinyl)pyridine (4e)**




A solution of 1-([1,1'-biphenyl]-4-yl)-1-(pyridin-2-yl)ethan-1-ol (**S4**) (1.00 g, 3.63 mmol, 1.00 equiv) in $CH_2Cl_2$ (18.2 mL, 0.200 M) was cooled to 0 °C. Triethylamine (1.47 g, 2.02 mL, 14.5 mmol, 4.00 equiv) and methanesulfonyl chloride (1.25 g, 0.843 mL, 10.9 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 4:1 (v/v)), to afford the title compound as a white solid (0.493 g, 1.92 mmol, 53% yield).

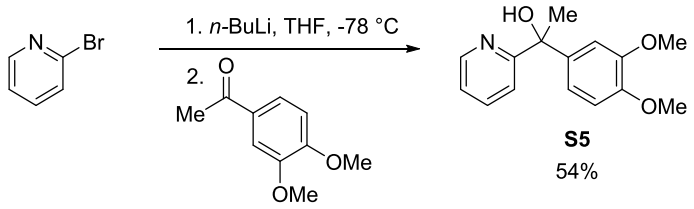
**$R_f$** = 0.59 (hexanes:EtOAc 4:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.70–8.67 (m, 1H), 7.67 (td, *J* = 7.7, 1.7 Hz, 1H), 7.65–7.60 (m, 4H), 7.49–7.44 (m, 4H), 7.39–7.35 (m, 2H), 7.24 (dd, *J* = 7.5, 4.5 Hz, 1H), 6.01 (s, 1H), 5.70 (s, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 158.7, 149.5, 148.9, 140.9, 140.8, 139.4, 136.5, 128.9, 128.9, 127.4, 127.2, 127.1, 123.0, 122.6, 117.8.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{19}H_{16}N$ ($[M + H]^+$): 258.1277, found: 258.128.

**1-(3,4-Dimethoxyphenyl)-1-(pyridin-2-yl)ethan-1-ol (S5)**




A solution of 2-bromopyridine (2.37 g, 1.43 mL, 15.0 mmol, 1.00 equiv) in THF (18.8 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (15.8 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 3′,4′-dimethoxyacetophenone (2.70 g, 15.0 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 to 4:2 (v/v)), to afford the title compound as yellow oil (2.08 g, 8.03 mmol, 54% yield).

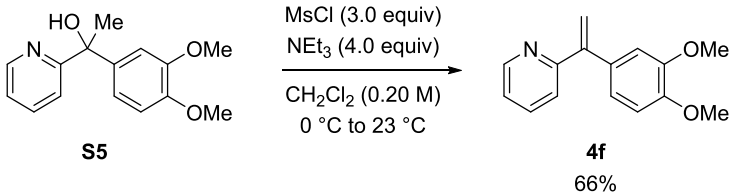
**$R_f$** = 0.22 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.51 (d, *J* = 4.8 Hz, 1H), 7.64 (td, *J* = 7.7, 1.7 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 7.3, 4.7 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.97 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.83 (br. s, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 1.90 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 165.0, 148.8, 148.1, 147.4, 139.9, 137.1, 122.1, 120.3, 118.0, 110.6, 109.7, 75.0, 55.9, 55.9, 29.5.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{18}NO_3$ ($[M + H]^+$): 260.1281, found: 260.1286.

**2-(1-(3,4-Dimethoxyphenyl)vinyl)pyridine (4f)**



A solution of 1-(3,4-dimethoxyphenyl)-1-(pyridin-2-yl)ethan-1-ol (**S5**) (1.00 g, 3.86 mmol, 1.00 equiv) in $CH_2Cl_2$ (19.3 mL, 0.200 M) was cooled to 0 °C. Triethylamine (1.56 g, 2.15 mL, 15.4 mmol, 4.00 equiv) and methanesulfonyl chloride (1.33 g, 0.896 mL, 11.6 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 3:2 (v/v)), to afford the title compound as a yellow (0.616 g, 2.55 mmol, 66% yield).

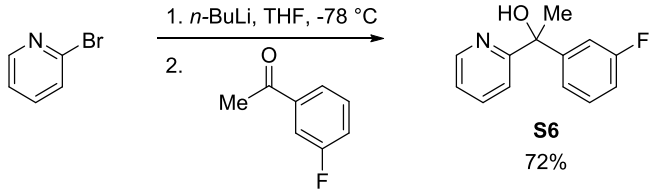
$\mathbf{R_f}$ = 0.36 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.63 (d, *J* = 4.8 Hz, 1H), 7.62 (td, *J* = 7.6, 1.9 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.90–6.87 (m, 2H), 6.86–6.83 (m, 1H), 5.87 (d, *J* = 1.1 Hz, 1H), 5.55 (d, *J* = 1.0 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 158.9, 149.4, 149.0, 148.9, 148.7, 136.4, 133.2, 123.0, 122.5, 121.1, 116.8, 111.7, 111.0, 56.0, 55.9.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{16}NO_2$ ($[M + H]^+$): 242.1176, found: 242.1179.

**1-(3-Fluorophenyl)-1-(pyridin-2-yl)ethan-1-ol (S6)**




A solution of 2-bromopyridine (3.16 g, 1.91 mL, 20.0 mmol, 1.00 equiv) in THF (25.0 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (21.0 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 3-fluoroacetophenone (2.76 g, 2.45 mL, 20.0 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (25.0 mL) and EtOAc (25.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 25.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 17:3 (v/v)), to afford the title compound as a yellow oil (3.13 g, 14.4 mmol, 72% yield).

$\mathbf{R_f}$ = 0.58 (hexanes:EtOAc 7:3 (v/v)).

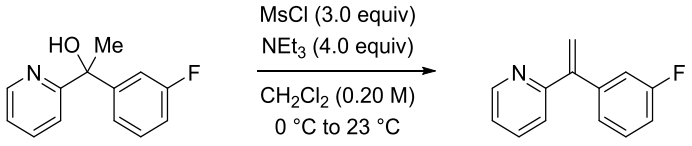
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.53–8.51 (d, *J* = 4.6 Hz, 1H), 7.66 (td, *J* = 7.7, 1.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.29–7.23 (m, 2H), 7.22–7.18 (m, 2H), 6.93–6.88 (m, 1H), 5.89 (s, 1H), 1.91 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 164.13, 162.92 (d, *J* = 245.3 Hz), 150.09 (d, *J* = 6.4 Hz), 147.62, 137.28, 129.78 (d, *J* = 7.8 Hz), 122.40, 121.58 (d, *J* = 2.0 Hz), 120.26, 113.95 (d, *J* = 21.3 Hz), 113.28 (d, *J* = 22.2 Hz), 74.91, 29.24.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –113.6 (s).

**HRMS** (ESI-TOF) (m/z): calcd for $C_{13}H_{13}FNO$ ($[M + H]^+$): 218.0976, found: 218.0979.

**2-(1-(3-Fluorophenyl)vinyl)pyridine (4g)**




**S6** **4g** 48%

A solution of 1-(3-fluorophenyl)-1-(pyridin-2-yl)ethan-1-ol (**S6**) (1.00 g, 4.60 mmol, 1.00 equiv) in $CH_2Cl_2$ (23.0 mL, 0.200 M) was cooled to 0 °C. Triethylamine (1.86 g, 2.56 mL, 28.4 mmol, 4.00 equiv) and methanesulfonyl chloride (1.58 g, 1.07 mL, 13.8 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 38 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 (v/v)), to afford the title compound as a yellow oil (0.436 g, 2.19 mmol, 48% yield).

$\mathbf{R}_f$ = 0.76 (hexanes:EtOAc 4:1 (v/v)).

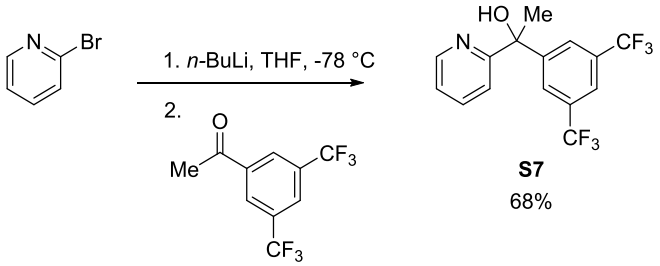
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.68–8.61 (m, 1H), 7.70–7.62 (m, 1H), 7.34–7.28 (m, 2H), 7.25–7.22 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.06 (dt, *J* = 9.9, 2.2 Hz, 1H), 7.03 (td, *J* = 8.4, 2.6 Hz, 1H), 6.03–5.97 (m, 1H), 5.68–5.61 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 162.9 (d, *J* = 244.1 Hz), 158.1, 149.6, 148.3, 142.6 (d, *J* = 7.4 Hz), 136.7, 129.9 (d, *J* = 8.5 Hz), 124.3, 124.3, 122.9 (d, *J* = 27.0 Hz), 118.7, 115.5 (d, *J* = 21.6 Hz), 114.9 (d, *J* = 20.9 Hz).

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –113.9.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{13}H_{11}FN$ ($[M + H]^+$): 200.0870, found: 200.0873.

**1-(3,5-Bis(trifluoromethyl)phenyl)-1-(pyridin-2-yl)ethan-1-ol (S7)**




**S7** 68%

A solution of 2-bromopyridine (1.34 g, 0.808 mL, 8.47 mmol, 1.00 equiv) in THF (10.6 mL, 0.800 M) was cooled to -78 °C. *n*-Butyllithium (8.89 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-one (2.17 g, 1.53 mL, 8.47 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for

15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford the title compound as a brown oil (1.93 g, 5.76 mmol, 68% yield).

**$R_f$** = 0.62 (hexanes:EtOAc 4:1 (v/v)).

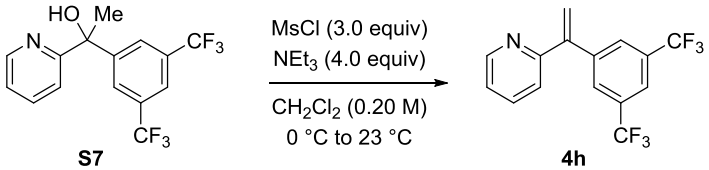
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.55 (d, *J* = 4.5 Hz, 1H), 7.97 (s, 2H), 7.75–7.71 (m, 2H), 7.34 (d, *J* = 7.74 Hz, 1H), 7.27–7.24 (m, 1H), 5.97 (s, 1H), 1.97 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 162.92, 150.18, 148.07, 137.73, 131.61 (q, *J* = 33.1), 126.32 (d, *J* = 1.8 Hz), 123.5 (q, *J* = 280.9 Hz), 122.94, 121.23 (t, *J* = 3.6 Hz), 120.06, 74.93, 29.36.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –63.3 (s).

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{12}F_6NO$ ($[M + H]^+$): 336.0818, found: 336.0821.

**2-(1-(3,5-Bis(trifluoromethyl)phenyl)vinyl)pyridine (4h)**




A solution of 1-(3,5-bis(trifluoromethyl)phenyl)-1-(pyridin-2-yl)ethan-1-ol (**S7**) (1.00 g, 2.98 mmol, 1.00 equiv) in $CH_2Cl_2$ (14.9 mL, 0.200 M) was cooled to 0 °C. Triethylamine (1.21 g, 1.66 mL, 11.9 mmol, 4.00 equiv) and methanesulfonyl chloride (1.02 g, 0.692 mL, 8.94 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 38 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (40.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (19:1 to 9:1 (v/v)), to afford the title compound as a yellow oil (0.334 g, 1.05 mmol, 35% yield).

**$R_f$** = 0.65 (hexanes:EtOAc 4:1 (v/v)).

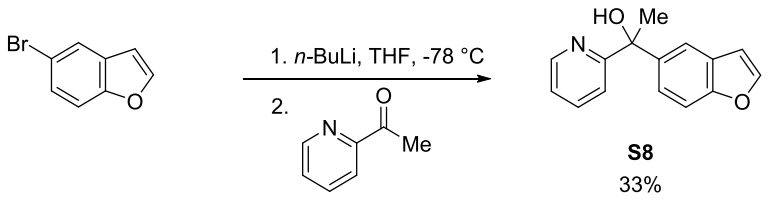
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.64 (d, *J* = 4.8 Hz, 1H), 7.85 (s, 1H), 7.81 (s, 2H), 7.74 (td, *J* = 7.7, 2.2 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 7.5, 4.5 Hz, 1H), 6.08 (s, 1H), 5.74 (s, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 157.2, 149.7, 147.2, 142.5, 137.1, 131.7 (q, *J* = 33.2 Hz), 128.7, 123.4 (q, *J* = 271.1 Hz), 123.3, 122.6, 121.8 (m), 120.4.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –63.4.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{10}F_6N$ ($[M + H]^+$): 318.0712, found: 318.0716.

**1-(Benzofuran-5-yl)-1-(pyridin-2-yl)ethan-1-ol (S8)**




A solution of 5-bromobenzofuran (2.01 g, 10.2 mmol, 1.00 equiv) in THF (34.0 mL, 0.300 M) was cooled to -78 °C. *n*-Butyllithium (10.2 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 2-acetylpyridine (1.24 g, 01.14 mL, 10.2 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for 15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (40.0 mL) and EtOAc (30.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 30.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (15:3 to 7:3 (v/v)), to afford the title compound as a yellow oil (0.799 g, 3.34 mmol, 33% yield).

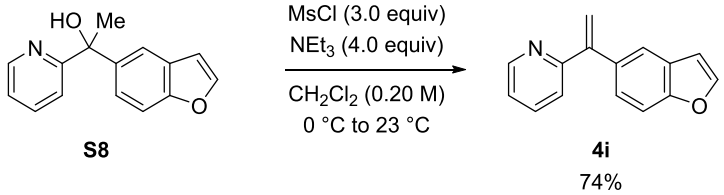
$\mathbf{R_f}$ = 0.60 (hexanes:EtOAc 2:3 (v/v)).

**$^1$H NMR** (400 MHz, $CDCl_3$, δ): 8.53 (q, *J* = 1.8 Hz, 1H), 7.75 (d, *J* = 1.1 Hz, 1H), 7.63 (td, *J* = 7.7, 1.9 Hz, 1 H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.42 (q, *J* = 4.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1 H), 6.73 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1 H), 5.89 (br. s, 1H), 1.99 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$, δ): 165.2, 154.1, 147.5, 145.4, 142.0, 137.1, 127.3, 123.0, 122.1, 120.5, 118.6, 111.1, 106.9, 75.3, 29.8.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{14}NO_2$ ($[M + H]^+$): 240.1019, found: 240.1022.

**1-(Benzofuran-5-yl)-1-(pyridin-2-yl)ethan-1-ol (4i)**




A solution of 1-(benzofuran-5-yl)-1-(pyridin-2-yl)ethan-1-ol (**S8**) (0.769 g, 3.21 mmol, 1.00 equiv) in $CH_2Cl_2$ (16.1 mL, 0.200 M) was cooled to 0 °C. Triethylamine (1.30 g, 1.80 mL, 12.8 mmol, 4.00 equiv) and methanesulfonyl chloride (1.10 g, 0.745 mL, 9.63 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (30.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (4:1 to 7:3 (v/v)), to afford the title compound as a light brown oil (0.523 g, 2.36 mmol, 74% yield).

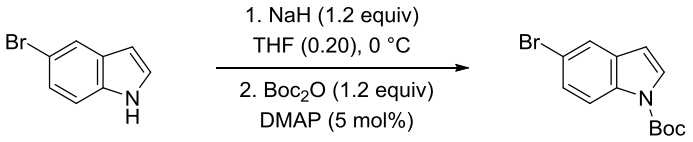
$\mathbf{R_f}$ = 0.62 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 4.3 Hz 1H), 7.65–7.61 (m, 2H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.31–7.27 (m, 2H), 7.21 (dd, *J* = 7.5, 4.5 Hz, 1H), 6.75 (d, *J* = 1.2 Hz, 1H), 6.01 (d, *J* = 1.0 Hz, 1H), 5.62 (d, *J* = 0.9 Hz, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 159.1, 154.8, 149.5, 149.4, 145.6, 136.4, 135.5, 127.6, 125.2, 123.0, 122.5, 121.3, 117.6, 111.2, 106.9.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{15}H_{12}NO$ ($[M + H]^+$): 222.0913, found: 222.0916.

***tert*-Butyl 5-bromo-1*H*-indole-1-carboxylate (S9)**




**S9**
91%

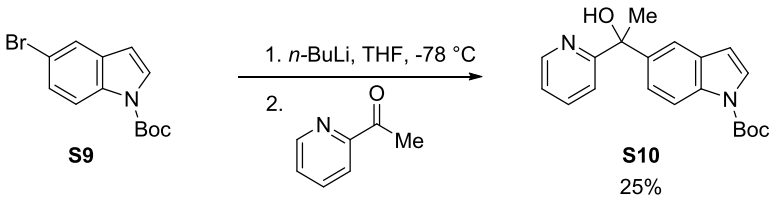
A solution of 5-bromoindole (2.00 g, 10.2 mmol, 1.00 equiv) in THF (51.0 mL, 0.200 M) was cooled to 0 °C. NaH (60% dispersion in mineral oil) (490 mg, 12.2 mmol, 1.20 equiv) was then added and the reaction mixture was stirred at 0 °C for 1 h. After that time, Boc anhydride (2.67 g, 12.2 mmol, 1.20 equiv) and 4-dimethylaminopyridine (62.3 mg, 0.510 mmol, 5 mol%) were added and the reaction mixture was stirred for 12 h while warming up to 23 °C. $NH_4Cl$(aq) (50.0 mL) and EtOAc (50.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 40.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (9:1 (v/v)), to afford the title compound as a white solid (2.74 g, 9.27 mmol, 91% yield).

**$R_f$** = 0.80 (hexanes:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.03 (br. s, 1 H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.62–7.57 (br. s, 1H), 7.40 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.50 (d, *J* = 3.9 Hz, 1H), 1.67 (s, 9H). (Note: Only ten peaks were observed probably due to accidental overlap of two peaks).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 149.5, 134.0, 132.3, 127.1, 123.6, 116.7, 116.1, 106.6, 84.2, 28.3.

***tert*-Butyl 5-(1-hydroxy-1-(pyridin-2-yl)ethyl)-1*H*-indole-1-carboxylate (S10)**




**S9** **S10**
25%

A solution of *tert*-butyl 5-bromo-1*H*-indole-1-carboxylate (**S9**) (2.00 g, 6.75 mmol, 1.00 equiv) in THF (22.5 mL, 0.300 M) was cooled to -78 °C. *n*-Butyllithium (7.08 mmol, 1.05 equiv) was then slowly added and the reaction mixture was stirred at -78 °C for 10 min. After that time, 2-acetylpyridine (0.818 g, 0.757 mL, 6.75 mmol, 1.00 equiv) was added to the above solution and the reaction mixture was stirred for

15 h while slowly warming up to 23 °C. $NH_4Cl$(aq) (20.0 mL) and EtOAc (20.0 mL) were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (7:3 (v/v)), to afford the title compound as a pink solid (0.569 g, 1.68 mmol, 25% yield).

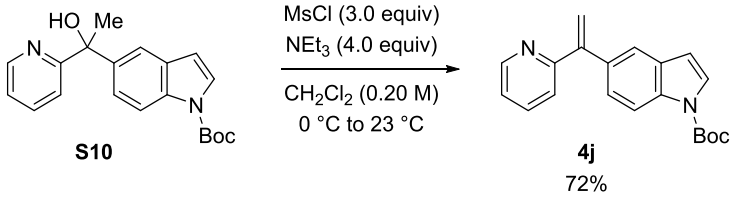
**$R_f$** = 0.46 (hexanes:EtOAc 7:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.53 (d, *J* = 4.6 Hz, 1H), 8.12–7.98 (m, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.62 (td, *J* = 7.7, 1.7 Hz, 1H), 7.59 –7.51 (m, 1H), 7.40 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.54 (d, *J* = 3.9 Hz, 1H), 5.97–5.78 (m, 1H), 1.99 (s, 3H), 1.65 (s, 9H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 165.3, 149.9, 147.4, 141.8, 137.2, 134.3, 130.6, 126.4, 122.8, 122.1, 120.5, 118.3, 115.0, 107.7, 83.8, 75.3, 29.7, 28.3.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{23}N_2O_3$ ($[M + H]^+$): 339.1703, found: 339.1707.

***tert*-Butyl 5-(1-(pyridin-2-yl)vinyl)-1*H*-indole-1-carboxylate (4j)**




A solution of *tert*-butyl 5-(1-hydroxy-1-(pyridin-2-yl)ethyl)-1*H*-indole-1-carboxylate (**S10**) (0.535 g, 1.58 mmol, 1.00 equiv) in $CH_2Cl_2$ (7.90 mL, 0.200 M) was cooled to 0 °C. Triethylamine (0.640 g, 0.881 mL, 6.32 mmol, 4.00 equiv) and methanesulfonyl chloride (0.543 g, 0.367 mL, 4.74 mmol, 3.00 equiv) were then added and the reaction mixture was stirred for 15 h while warming up to 23 °C. Saturated solution of $NaHCO_3$(aq) (20.0 mL) was added, the layers were separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20.0 mL). The organic extracts were combined, dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with hexanes:EtOAc (17:3 to 4:1 (v/v)), to afford the title compound as a yellow oil (0.366 g, 1.14 mmol, 72% yield).

**$R_f$** = 0.65 (hexanes:EtOAc 7:3 (v/v)).

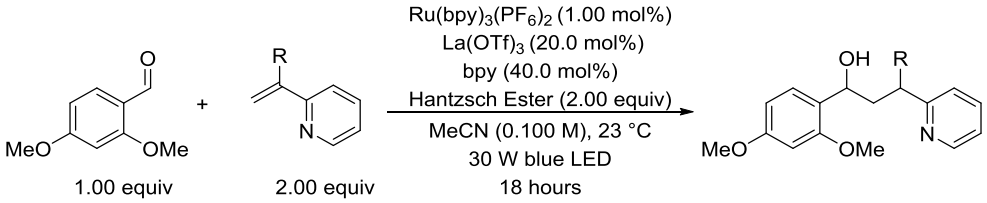
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 4.7 Hz, 1H), 8.11 (br. s, 1H), 7.64–7.59 (m, 2H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.21 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.55 (d, *J* = 3.9 Hz, 1H), 6.01 (s, 1H), 5.63 (s, 1H), 1.68 (s, 9H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 159.1, 149.8, 149.5, 149.5, 136.4, 135.2, 134.9, 130.8, 126.5, 125.0, 123.1, 122.5, 121.0, 117.5, 115.0, 107.6, 83.9, 28.3.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{21}N_2O_2$ ($[M + H]^+$): 321.1598, found: 321.1603.

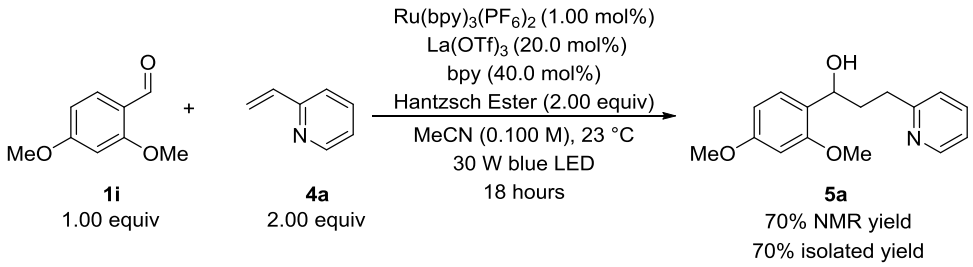
# Coupling of 2,4-Dimethoxybenzaldehyde with 2-Vinylpyridines

**General Procedure (based on 0.15 mmol scale unless otherwise stated)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (20.0 mol%) and bipyridine (40.0 mol%). MeCN (0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (1.00 equiv), 2-vinylpyridine (2.00 equiv), Hantzsch Ester (2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (30 W, 455 nm unless otherwise stated). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:1 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc for development was needed in a few cases to afford pure products.

**1-(2,4-Dimethoxyphenyl)-3-(pyridin-2-yl)propan-1-ol (5a)**



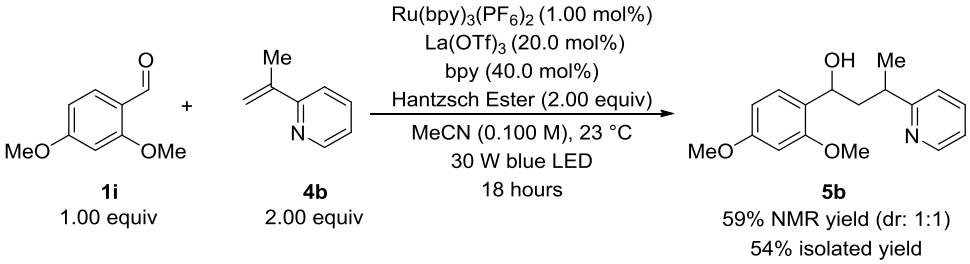

In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-vinylpyridine (**4a**) (58.6 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source ($\lambda$ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a colorless oil (28.7 mg, 0.105 mmol, 70% yield). $\mathbf{R}_f$ = 0.31 (Hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.3 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 6.1 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 4.97 (dd, *J* = 4.4, 7.6 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 2.98 (m, 1H), 2.91 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 161.97, 159.97, 157.43, 148.79, 136.76, 127.66, 125.59, 123.30, 121.16, 104.06, 98.61, 69.54, 55.49, 55.39, 36.31, 34.87.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{16}H_{20}NO_3$ ($[M + H]^+$): 274.1453, found: 274.1453.

**1-(2,4-Dimethoxyphenyl)-3-(pyridin-2-yl)butan-1-ol (5b)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(prop-1-en-2-yl)pyridine (**4b**) (35.8 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (1:4 (v/v)) to afford the title compound as a colorless oil (23.3 mg, 0.0810 mmol, 54% yield).

Reported as diastereomers:

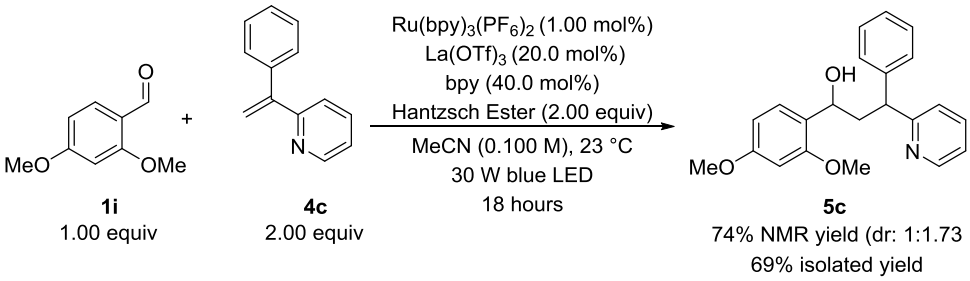
**$R_f$** = 0.37 (hexanes:EtOAc 1:4 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.54 (d, *J* = 2.3 Hz, 1H), 7.66 – 7.59 (m, 1H), 7.28 and 7.18 (d, *J* = 8.4 Hz, 1H, d, *J* = 7.38 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.45 and 6.41 (d, *J* = 8.61 Hz, 1H, d, *J* = 26.4 Hz, 2H), 4.89 and 4.75 (dd, *J* = 4.7, 8.8 Hz, 1H, dd, *J* = 3.58, 8.83 Hz, 1H), 3.80 and 3.78 (s, 3H), 3.79 and 3.75 (s, 3H), 3.23 and 3.14 (m, 1H, q, *J* = 6.9 Hz, 1H), 2.25 and 2.15 (m, 1H), 2.08 – 1.98 (m, 1H), 1.36 and 1.34 (d, *J* = 2.8 Hz, 1H, d, *J* = 2.8 Hz, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 166.43, 165.92, 160.06, 159.88, 157.66, 157.31, 148.84, 148.71, 104.11, 104.09, 98.73, 98.57, 69.16, 67.05, 55.50, 55.48, 55.38, 55.35, 21.21, 20.96.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{17}H_{22}NO_3$ ($[M + H]^+$): 288.1596, found: 288.1596.

**1-(2,4-Dimethoxyphenyl)-3-phenyl-3-(pyridin-2-yl)propan-1-ol (5c)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-phenylvinyl)pyridine (**4c**) (54.3 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:1.6 mixture of diastereomers (36.0 mg, 0.103 mmol, 69% yield) as a white solid.

Reported as Diastereomers:

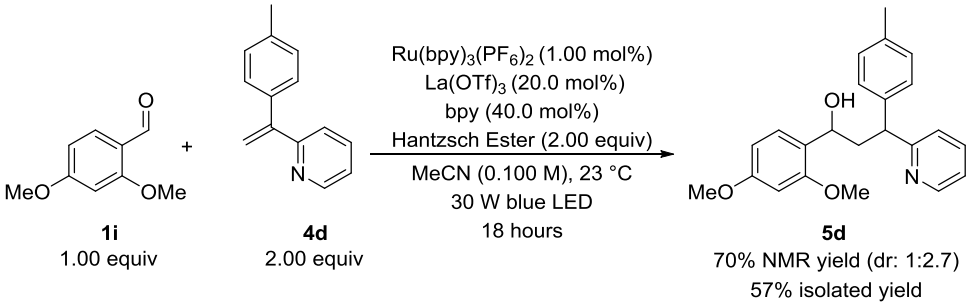
$\mathbf{R_f}$ = 0.15 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.60 and 8.58 (d, *J* = 4.6 Hz, 1H), 7.59 and 7.56 (t, *J* = 7.6 Hz, 1H, t, *J* = 7.6 Hz, 1H), 7.41 – 7.09 (m, 8H), 6.47 (d, 1H), 6.43 (s, 1H), 4.79 and 4.74 (dd, *J* = 3.7, 9.2 Hz, 1H, dd, *J* = 3.9, 8.3 Hz, 1H), 4.43 and 4.37 (t, *J* = 7.3 Hz, 1H, dd, *J* = 4.8, 9.5 Hz, 1H), 3.81 (s, 3H), 3.77 and 3.74 (s, 3H, s, 3H), 2.78 and 2.68 (m, 1H, m, 1H), 2.55 and 2.51 (m,1H, m,1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 164.15, 163.47, 160.02, 159.98, 157.59, 157.49, 148.89, 148.76, 144.09, 136.70, 136.56, 128.62, 128.56, 128.51, 128.35, 127.79, 127.46, 126.48, 125.28, 123.72, 121.44, 121.34, 104.02, 98.67, 9.00, 68.05, 55.49, 55.46, 55.28, 50.97, 50.19, 43.08,42.31.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{22}H_{24}NO_3$ ($[M + H]^+$): 350.1754, found: 350.1754.

**1-(2,4-Dimethoxyphenyl)-3-(pyridin-2-yl)-3-(*p*-tolyl)propan-1-ol (5d)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-(*p*-tolyl)vinyl)pyridine (**4d**) (58.6 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:2.7 mixture of diastereomers (31.1 mg, 0.0855 mmol, 57% yield) as a white solid.

The $^1$H NMR are recorded in a mixture of two diastereomers. The two diastereomers were not separated by Preparative TLC. Based on their ratio in the $^1$H NMR and the difference between chemical shifts, the chemical shifts and integrals are assigned to each diastereomer. $^{13}$C NMR is reported as the mixture of two diastereomers.

Data for diastereomer 1:

$\mathbf{R_f}$ = 0.12 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.11 (m, 5H), 6.44 (dd, *J* = 8.29, 2.13 Hz, 1H), 6.41 (s, 1H), 4.71 (dd, *J* = 8.26, 3.99 Hz, 1H), 4.30 (dd, *J* = 9.34, 4.86 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 2.73 (m, 1H), 2.46 (m, 1H), 2.30 (s, 3H).

Data for diastereomer 2:

$\mathbf{R_f}$ = 0.12 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

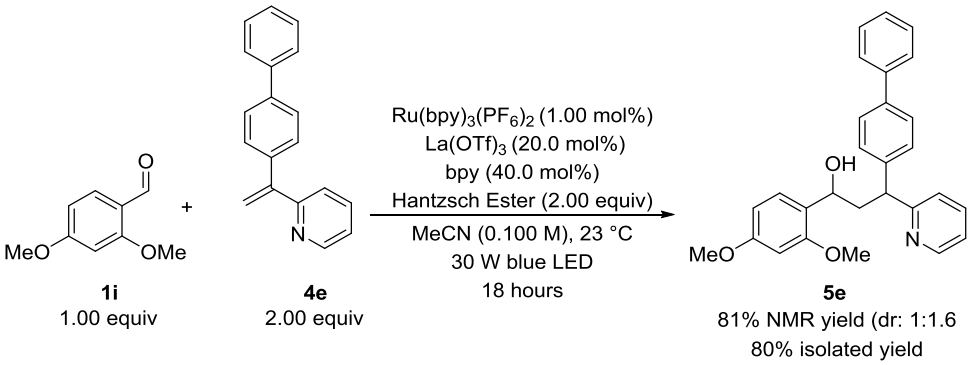
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 10.3 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 3H), 7.11 (m, 5H), 6.44 (m, 1H), 6.41 (s, 1H), 4.76 (dd, *J* = 9.20, 3.6 Hz, 1H), 4.37 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.64 (m, 3H), 2.51 (q, 3H), 2.31 (s, 3H).

Reported as diastereomers.

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 164.39, 163.72, 160.03, 159.98, 157.62, 157.51, 148.67, 141.07, 140.84, 136.78, 136.70, 136.11, 136.03, 129.36, 129.30, 128.37, 128.22, 127.84, 127.49, 125.32, 123.68, 123.43, 121.41, 121.32, 104.03, 98.69, 69.05, 68.16, 55.49, 55.31, 50.53, 49.78, 43.09, 42.34, 21.15.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{23}H_{26}NO_3$ ($[M + H]^+$): 364.1912, found: 364.1912.

**3-([1,1'-Biphenyl]-4-yl)-1-(2,4-dimethoxyphenyl)-3-(pyridin-2-yl)propan-1-ol (5e)**




**1i** 1.00 equiv

**4e** 2.00 equiv

**5e** 81% NMR yield (dr: 1:1.6) 80% isolated yield

In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-([1,1'-biphenyl]-4-yl)vinyl)pyridine (**4e**) (77.2 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:1.6 mixture of diastereomers (51.7 mg, 0.121 mmol, 80% yield) as a white solid. Diastereomers were not completely separated by Preparative TLC (Hexanes:EtOAc, 4:1 (v/v)), however, the front portion of the TLC plates contained more diastereomer 1 and the portion after it was a mixture of two diastereomers.

Characterizations of diastereomer 1 is based on the isolated single isomer. Characterization of diastereomer 2 is completed by comparing the spectrum of a mixture of two diastereomers to the isolated diastereomer 1.

Data for diastereomer 1:

**$R_f$** = 0.11 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.2 Hz, 1H), 7.59 (m, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.14 (q, *J* = 3.9 Hz, 1H), 6.45 (dd, *J* = 2.3, 8.4 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 4.73 (dd, *J* = 4.0, 8.5 Hz, 1H), 4.38 (dd, *J* = 4.8, 9.3 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.78 (m, 1H), 2.52 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 163.36, 160.03, 157.54, 148.89, 143.18, 141.03, 139.37, 136.80, 128.82, 128.75, 127.83, 127.30, 127.21, 127.12, 125.21, 123.77, 121.54, 104.06, 98.71, 68.17, 55.49, 55.32, 49.87, 42.34.

Data for diastereomer 2:

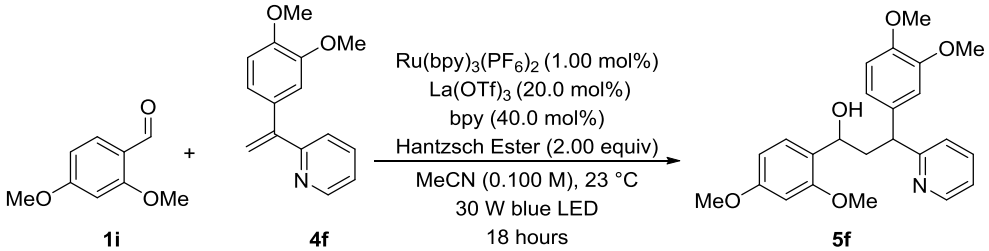
**$R_f$** = 0.11 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.6 Hz, 1H), 7.59 (m, 5H), 7.42 (m, 3H), 7.34 (m, 2H), 7.32 (m, 2H), 7.23 (t, *J* = 6.9 Hz, 1H), 7.14 (m, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 6.45 (q, *J* = 3.9 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 4.80 (d, *J* = 3.4 Hz, 1H), 4.78 (dd, *J* = 3.86, 8.46 Hz, 1H), 4.44 (t, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.68 (m, 1H), 2.57 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 164.08, 160.10, 157.65, 149.04, 142.97, 141.06, 139.44, 136.61, 128.92, 128.84, 127.85, 127.54, 127.36, 127.36, 127.14, 125.59, 123.47, 121.45, 104.09, 98.70, 69.13, 68.19, 56.13, 55.51, 55.34, 50.62, 43.04.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{28}H_{28}NO_3$ ($[M + H]^+$): 426.2069, found: 426.2069.

**1-(2,4-Dimethoxyphenyl)-3-(3,4-dimethoxyphenyl)-3-(pyridin-2-yl)propan-1-ol (5f)**




**1i** 1.00 equiv | **4f** 2.00 equiv | **5f** 84% NMR yield (dr: 1:1.8) 70% isolated yield

In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-(3,4-dimethoxyphenyl)vinyl)pyridine (**4f**) (72.4 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:1.6 mixture of diastereomers (43.0 mg, 0.101 mmol, 70% yield) as a white solid.

Reported as diastereomers:

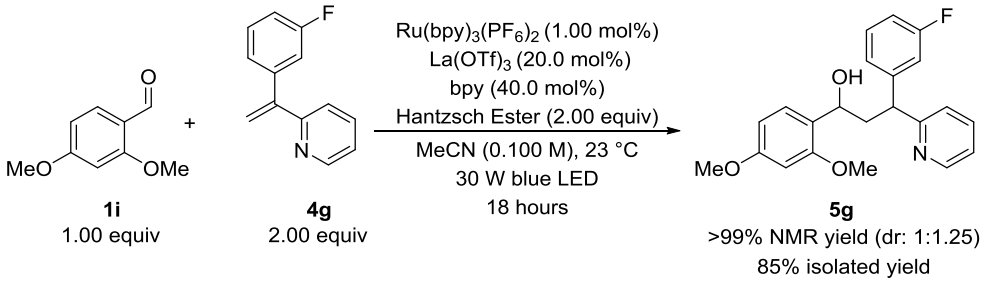
**$R_f$** = 0.1 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.56 and 8.55 (d, *J* = 4.5 Hz, 1H, d, *J* = 4.6 Hz, 1H), 7.57 and 7.55 (t, *J* = 7.7 Hz, 1H, t, *J* = 6.7 Hz, 1H), 7.22 and 7.21 (d, *J* = 8.5 Hz, 1H, d, *J* = 8.5 Hz, 1H), 7.12 (m, 1H), 6.91 and 7.69 (d, *J* = 8.2 Hz, 1H, m, 1H), 6.87 and 6.91 (s, 1H, m, 1H, ), 6.91 (m, 1H), 6.44 (m, 1H), 6.41 (s, 1H), 4.76 and 4.70 (dd, *J* = 3.5, 9.2 Hz, 1H, dd, *J* = 4.0, 8.3 Hz, 1H), 4.34 and 4.27 (t, *J* = 7.3 Hz, 1H dd, *J* = 4.9, 9.3 Hz, 1H), 3.85 and 3.83 (s, 3H, s, 3H), 3.83 and 3.82 (s, 3H, s, 3H), 3.79 (s, 3H), 3.75 and 3.72 (s, 3H, s, 3H), 2.72 and 2.63 (m, 1H), 2.50 and 2.46 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 164.37, 163.68, 160.06, 160.03, 157.63, 157.54, 149.05, 148.96, 148.74, 148.68, 147.73, 147.66, 136.81, 136.74, 136.68, 136.41, 127.89, 127.54, 125.67, 125.22, 123.59, 123.34, 121.46, 121.37, 120.42, 120.11, 111.68, 111.65, 111.17, 104.10, 104.05, 98.70, 68.99, 68.17, 55.98, 55.97, 55.50, 55.49, 55.34, 50.41, 49.74, 43.14, 42.45.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{24}H_{28}NO_5$ ($[M + H]^+$): 410.1966, found: 410.1966.

**1-(2,4-Dimethoxyphenyl)-3-(3-fluorophenyl)-3-(pyridin-4-yl)propan-1-ol (5g)**




**1i** 1.00 equiv | **4g** 2.00 equiv | **5g** >99% NMR yield (dr: 1:1.25) 85% isolated yield

In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 4-(1-(3-fluorophenyl)vinyl)pyridine (**4g**) (59.8 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:2.5 mixture of diastereomers (46.8 mg, 0.127 mmol, 85% yield) as a white solid.

Data for diastereomer 1:

$\mathbf{R}_f$ = 0.16 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.59 (t, *J* = 2.7 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.23 (m, *J* = 6.3 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 10.1 Hz, 1H), 6.88 (m, *J* = 3.7 Hz, 1H), 6.44 (q, *J* = 3.5 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 4.68 (dd, *J* = 3.96, 8.50 Hz, 1H), 4.37 (dd, *J* = 4.6, 9.17 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 2.73 (m, 1H), 2.46 (m, 1H), 1.62 (br. s, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 163.72, 162.70, 160.10, 157.50, 148.90, 136.96, 129.96, 129.91, 127.75, 124.03, 124.01, 123.77, 121.74, 115.33, 115.21, 113.47, 113.34, 104.11, 98.72, 67.96, 55.51, 55.32, 49.83, 42.26.

**$^{19}$F NMR** (376 MHz, $CDCl_3$): δ -115.4 (q, *J* = 7.9 Hz)

Data for diastereomer 2 :

**$R_f$** = 0.1 ($CH_2Cl_2$ :EtOAc 9:1 (v/v)).

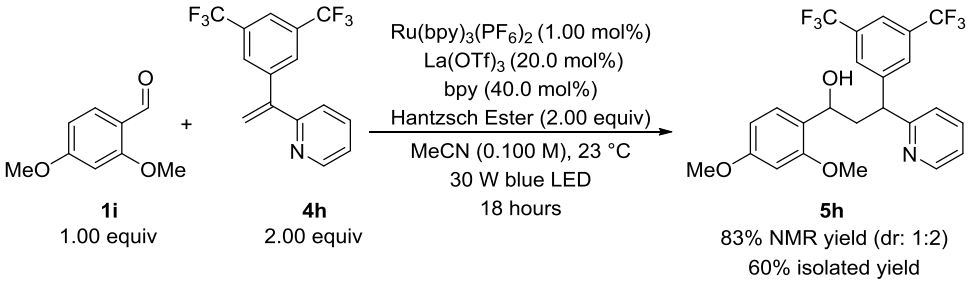
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.8 Hz, 2H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.25 (q, *J* = 12.6 Hz, 1H), 7.13 (q, *J* = 9.9 Hz, 4H), 6.90 (d, *J* = 1.8 Hz, 1H), 6.45 (dd, *J* = 2.27, 8.37 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 4.74 (dd, *J* = 3.57, 9.31 Hz, 1H), 4.46 (br. S, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.60 (q, *J* = 5.2 Hz, 1H), 2.53 (q, *J* = 4.1 Hz, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 163.80, 163.40, 162.41, 160.16, 157.57, 130.03, 129.99, 127.39, 125.41, 124.40, 123.41, 121.68, 115.40, 115.27, 113.62, 113.50, 104.12, 98.69, 68.78, 55.53, 55.32, 42.89.

**$^{19}$F NMR** ($CDCl_3$, 25 ºC, δ) : -115.3 (br.)

**HRMS** (ESI-TOF) (m/z): calcd for $C_{22}H_{23}FNO_3$ ($[M + H]^+$): 368.1660, found: 368.1660.

**3-(3,5-Bis(trifluoromethyl)phenyl)-1-(2,4-dimethoxyphenyl)-3-(pyridin-2-yl)propan-1-ol (5h)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-(3,5-bis(trifluoromethyl)phenyl)vinyl)pyridine (**4h**) (95.2 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:2 mixture of diastereomers (43.7 mg, 0.0900 mmol, 60% yield) as a white solid.

Reported as diastereomers:

**$R_f$** = 0.1 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

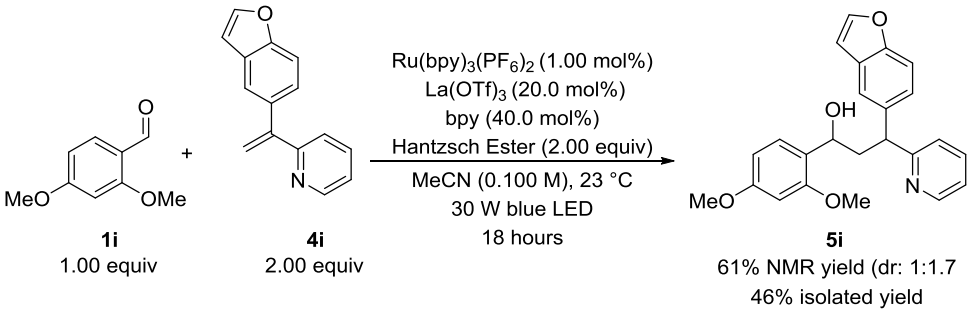
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.61 and 8.57 (d, *J* = 4.8 Hz, 1H, d, *J* = 4.7 Hz, 1H), 7.89 and 7.78 (s, 2H, s, 2H), 7.69 (s, 1H), 7.63 and 7.60 (t, *J* = 7.8 Hz, 1H, t, *J* = 7.4 Hz, 1H), 7.22 – 7.16 and 7.22 – 7.11 (m, 3H), 6.46 – 6.42 (m, 1H), 6.40 and 6.38 (d, *J* = 2.2, 1H, d, *J* = 3.15 Hz, 1H), 4.65 and 4.50 (dd, *J* = 4.4, 9.4 Hz, 1H, dd, *J* = 4.9, 9.5 Hz, 1H), 4.52 and 4.50 (dd, *J* = 5.2, 9.2 Hz, 1H, dd, *J* = 4.9, 9.5 Hz, 1H), 3.79 and 3.78 (s, 3H), 3.74 and 3.73 (s, 3H), 2.78 and 2.63 (m, 1H, m, 1H), 2.56 and 2.47 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 162.14, 161.31, 160.32, 157.50, 157.37, 149.56, 146.62, 137.12, 137.05, 131.57 (q, *J* = 33.0 Hz), 128.88, 128.58, 127.64, 127.20, 124.85, 124.52, 124.30, 123.72, 123.07, 122.75, 122.17, 122.04, 120.57, 104.25, 104.18, 98.74, 98.62, 55.51, 55.50, 55.31, 55.22, 50.25, 49.74, 42.85, 42.61.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ) : -62.63, -62.70.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{24}H_{22}F_6NO_3$ ($[M + H]^+$): 486.1502, found: 486.1502.

**3-(Benzofuran-5-yl)-1-(2,4-dimethoxyphenyl)-3-(pyridin-2-yl)propan-1-ol (5i)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), 2-(1-(benzofuran-5-yl)vinyl)pyridine (**4i**) (66.4 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:1.6 mixture of diastereomers (26.9 mg, 0.069 mmol, 46% yield) as a white solid.

Data for diastereomers:

**$R_f$** = 0.20 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

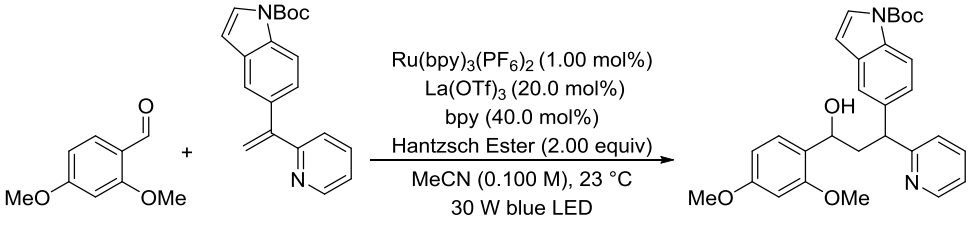
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.58 and 8.56 (d, *J* = 4.8 Hz, 1H, d, *J* = 4.8 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.43 and 7.40 (d, *J* = 9.4 Hz, 1H, d, *J* = 8.5 Hz, 1H), 7.30 – 7.19 (m, *J* = 5.1 Hz, 2H), 7.18 – 7.06 (m, 2H), 6.71 and 6.69 (d, *J* = 1.1 Hz, 1H, d, *J* = 1.2 Hz, 1H), 6.45 (m, 1H), 6.41 (q, 1H), 4.77 and 4.73 (dd, *J* = 3.5,

9.3 Hz, 1H, dd, *J* = 4.1, 8.2 Hz, 1H), 4.52 and 4.43 (*J* = 7.3 Hz, 1H, dd, *J* = 4.9, 9.3 Hz, 1H), 3.79 and 3.78 (s, 1H, s, 3H), 3.74 and 3.70 (s, 1H, s, 3H), 2.80 and 2.69 (m, 1H, m, 1H), 2.57 and 2.53 (m, 1H, m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 164.54, 163.86, 160.03, 159.99, 157.61, 157.51, 153.98, 153.88, 148.92, 148.77, 145.30, 138.72, 138.49, 136.73, 136.58, 127.83, 127.70, 127.66, 127.46, 125.74, 125.30, 124.96, 123.73, 123.44, 121.42, 121.31, 120.87, 120.54, 111.38, 111.31, 106.75, 104.06,104.05, 98.69, 98.65, 68.96, 68.11, 56.11, 55.49, 55.30, 50.75, 50.05, 43.43, 42.71.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{24}H_{24}NO_4$ ($[M + H]^+$): 390.1704, found: 390.1704.

***tert*-Butyl 5-(3-(2,4-dimethoxyphenyl)-3-hydroxy-1-(pyridin-2-yl)propyl)-1*H*-indole-1-carboxylate (5j)**




In a glovebox, an oven-dried 4 mL vial was charged with $La(OTf)_3$ (17.6 mg, 0.0300 mmol, 20.0 mol%) and bipyridine (9.37 mg, 0.0600 mol, 40.0 mol%). MeCN (1.50 mL, 0.100 M, with respect to 2,4-methoxybenzaldehyde) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). 2,4-Methoxybenzaldehyde (**1i**) (24.9 mg, 0.150 mmol, 1.00 equiv.), *tert*-butyl 5-(1-(pyridin-2-yl)vinyl)-1*H*-indole-1-carboxylate (**4j**) (96.1 mg, 0.300 mmol, 2.00 equiv.), Hantzsch Ester (76.0 mg, 0.300 mmol, 2.00 equiv.), and $Ru(bpy)_3(PF_6)_2$ (1.29 mg, 1.50 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc (2:3 (v/v)). Further purification by preparative TLC using $CH_2Cl_2$:EtOAc (9:1 (v/v)) for development afforded the title compound as a 1:1.8 mixture of diastereomers (27.1 mg, 0.056 mmol, 37% yield) as a white solid.

Data for diastereomer 1:

**$R_f$** = 0.11 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.9 Hz, 1H), 8.05 (br. s, 1H), 7.57 (m, 2H), 7.47 (s, 1H), 7.25 (t, *J* = 8.76 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.14 (q, *J* = 5.90, 7.53 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.47 (dd, *J* = 2.3, 8.4 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 4.77 (dd, *J* = 4.2, 8.1 Hz, 1H), 4.44 (dd, *J* = 5.0, 9.2 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.83 (m, 1H), 2.57 (m, 1H), 1.67 (s, 9H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 163.98, 159.98, 157.50, 148.59, 138.49, 136.80, 127.87, 126.24, 125.33, 124.92, 123.75, 121.39, 120.39, 115.22, 107.47, 104.03, 98.69, 68.15, 55.32, 50.00, 42.53, 28.32.

Data for diastereomer 2:

**$R_f$** = 0.11 ($CH_2Cl_2$:EtOAc 9:1 (v/v)).

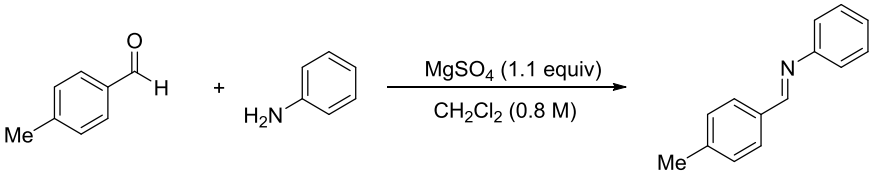
**$^1$H NMR** (700 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.8 Hz, 1H), 8.05 (br. s, 1H), 7.55 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.10 (m, 2H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.44 (dd, *J* = 2.2, 8.4 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 4.78 (dd, *J* = 3.3, 9.4 Hz, 1H), 4.54 (br. s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 2.69 (m, 1H), 2.58 (m, 1H), 1.65 (s, 9H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$) δ 160.03, 157.62, 127.44, 126.63, 126.27, 125.82, 124.95, 123.60, 121.35, 120.75, 115.32, 107.48, 104.05, 98.66, 69.02, 55.51, 55.33, 43.29, 28.33.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{29}H_{33}N_2O_5$ ($[M + H]^+$): 489.2388, found: 489.2388.

## Synthesis of Imine Substrates

### (*E*)-*N*-Phenyl-1-(*p*-tolyl)methanimine (6a)



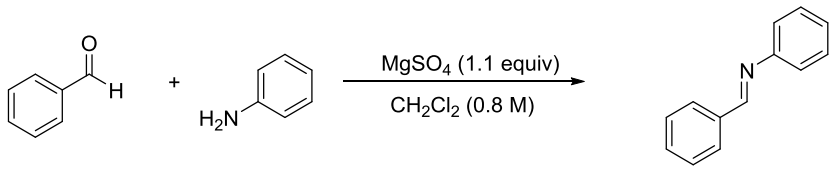

**6a**
53%

To a suspension of magnesium sulfate (1.99 g, 16.5 mmol, 1.10 equiv) in $CH_2Cl_2$ (18.8 mL, 0.800 M) was added 4-methylbenzaldehyde (1.77 mL, 1.80 g, 15.0 mmol, 1.00 equiv) and aniline (1.37 mL, 1.40 g, 15.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as an off-white solid (1.55 g, 7.93 mmol, 53% yield).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.43 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.42–7.37 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.25–7.20 (m, 3H), 2.43 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 160.5, 152.4, 142.0, 133.8, 129.7, 129.3, 129.0, 125.9, 121.0, 21.8.

### (*E*)-*N*,1-Diphenylmethanimine (6b)



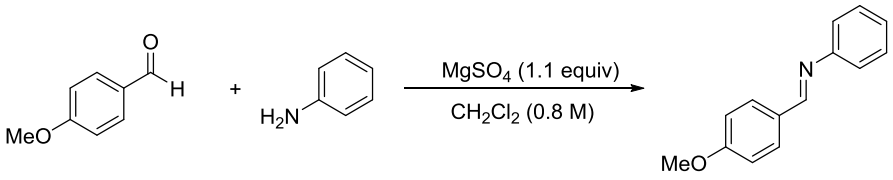

**6b**
52%

To a suspension of magnesium sulfate (3.97 g, 33.0 mmol, 1.10 equiv) in $CH_2Cl_2$ (37.5 mL, 0.800 M) was added benzaldehyde (3.05 mL, 3.18 g, 30.0 mmol, 1.00 equiv) and aniline (2.73 mL, 2.79 g, 30.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as a slightly yellow solid (2.81 g, 15.5 mmol, 52% yield).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.46 (s, 1H), 7.95–7.90 (m, 2H), 7.51–7.46 (m, 3H), 7.43–7.38 (m, 2H), 7.26–7.21 (m, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 160.5, 152.2, 136.3, 131.5, 129.3, 128.9, 128.9, 126.1, 121.0.

**(*E*)-1-(4-Methoxyphenyl)-*N*-phenylmethanimine (6c)**



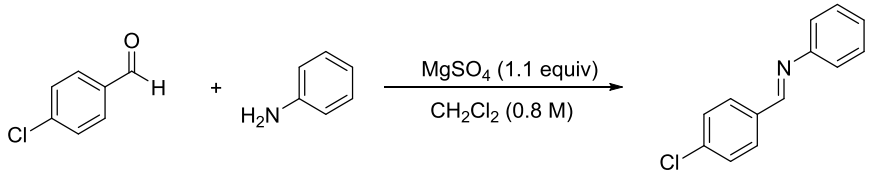

**6c**
70%

To a suspension of magnesium sulfate (3.97 g, 33.0 mmol, 1.10 equiv) in $CH_2Cl_2$ (37.5 mL, 0.800 M) was added 4-methoxybenzaldehyde (3.65 mL, 4.08 g, 30.0 mmol, 1.00 equiv) and aniline (2.73 mL, 2.79 g, 30.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as an off-white solid (4.43 g, 21.0 mmol, 70% yield).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.39 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.41–7.37 (m, 2H), 7.24–7.18 (m, 3H), 6.99 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 162.4, 159.9, 152.5, 130.7, 129.4, 129.2, 125.7, 121.0, 114.3, 55.6.

**(*E*)-1-(4-Chlorophenyl)-*N*-phenylmethanimine (6d)**



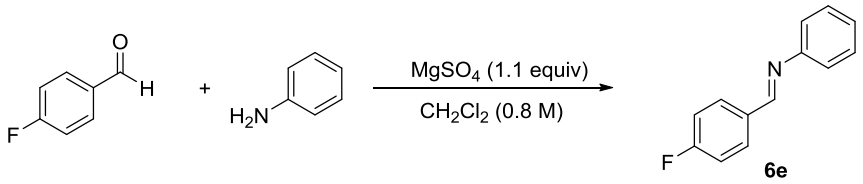

**6d**
70%

To a suspension of magnesium sulfate (3.97 g, 33.0 mmol, 1.10 equiv) in $CH_2Cl_2$ (37.5 mL, 0.800 M) was added 4-chlorobenzaldehyde (4.22 g, 30.0 mmol, 1.00 equiv) and aniline (2.73 mL, 2.79 g, 30.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as an off-white solid (4.53 g, 21.0 mmol, 70% yield).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.43 (s, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.28–7.24 (m, 1H), 7.24–7.21 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 159.0, 151.8, 137.5, 134.8, 130.1, 129.3, 129.2, 126.3, 121.0.

**(*E*)-1-(4-Fluorophenyl)-*N*-phenylmethanimine (6e)**




**6e**
60%

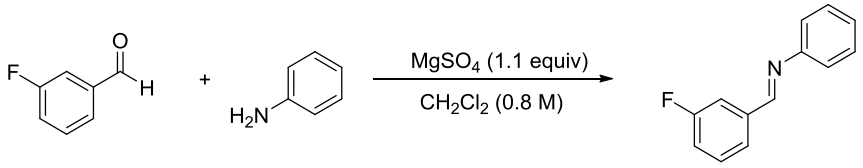
To a suspension of magnesium sulfate (3.97 g, 33.0 mmol, 1.10 equiv) in $CH_2Cl_2$ (37.5 mL, 0.800 M) was added 4-fluorobenzaldehyde (3.22 mL, 3.72 g, 30.0 mmol, 1.00 equiv) and aniline (2.73 mL, 2.79 g, 30.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as a white solid (3.60 g, 18.1 mmol, 60% yield).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.44 (s, 1H), 7.93 (dd, *J* = 8.60, 5.59 Hz, 2H), 7.46–7.40 (m, 2H), 7.29–7.25 (m, 1H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 8.6 Hz, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 164.8 (d, *J* = 250.6 Hz), 159.0, 152.0, 132.7 (d, *J* = 2.1 Hz), 130.9 (d, *J* = 8.7 Hz), 129.3, 126.2, 121.0, 116.1 (d, *J* = 21.7 Hz).

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –108.7.

**(*E*)-1-(3-Fluorophenyl)-*N*-phenylmethanimine (6f)**




**6f**
73%

To a suspension of magnesium sulfate (3.97 g, 33.0 mmol, 1.10 equiv) in $CH_2Cl_2$ (37.5 mL, 0.800 M) was added 3-fluorobenzaldehyde (3.18 mL, 3.72 g, 30.0 mmol, 1.00 equiv) and aniline (2.73 mL, 2.79 g, 30.0 mmol, 1.00 equiv) and the reaction mixture was stirred under nitrogen atmosphere at 23 °C for 15 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The crude product was recrystallized from hexanes by cooling the solution in a dry ice/acetone bath. Recrystallization afforded the title compound as a white solid (4.36 g, 21.9 mmol, 73% yield).

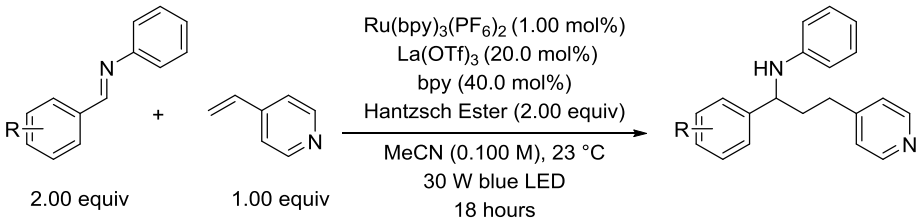
**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.44 (s, 1H), 7.68 (dt, *J* = 9.6, 2.10 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.44 (td, *J* = 8.0, 5.6 Hz, 1H), 7.42–7.39 (m, 2H), 7.28–7.24 (m, 1H), 7.24–7.21 (m, 2H), 7.18 (td, *J* = 8.4, 3.0 Hz, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 163.2 (d, *J* = 245.3 Hz), 158.9 (d, *J* = 2.4 Hz), 151.6, 138.7 (d, *J* = 7.2 Hz), 130.4 (d, *J* = 8.1 Hz), 129.4, 126.5, 125.0 (d, *J* = 2.0 Hz), 121.0, 118.4 (d, *J* = 21.5 Hz), 114.8 (d, *J* = 21.9 Hz).

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –113.1.

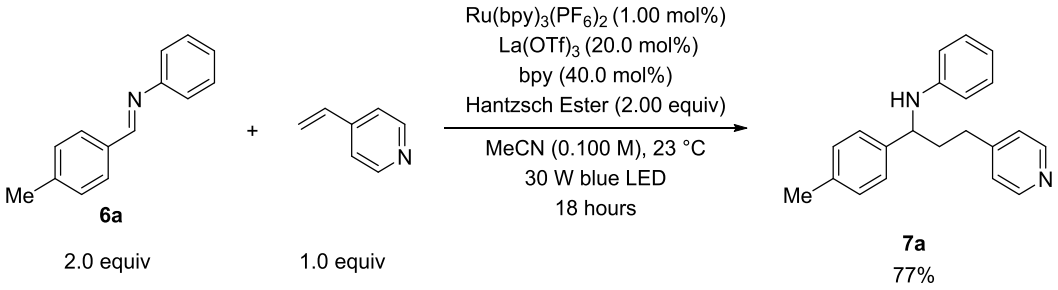
# Coupling of Imines with 4-Vinylpyridine

## General Procedure




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (20.0 mol%) and bipyridine (40.0 mol%). MeCN (0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). An imine substrate (2.00 equiv), 4-vinylpyridine (1.00 equiv), Hantzsch Ester (2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (30 W, 455 nm, unless otherwise stated). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue light. After that time, the reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel, eluting with hexanes:EtOAc, to afford the desired product.

### *N*-(3-(Pyridin-4-yl)-1-(*p*-tolyl)propyl)aniline (7a)




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (*E*)-*N*-Phenyl-1-(*p*-tolyl)methanimine (**6a**) (195 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 μL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source ($\lambda$ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 3:2 (v/v). The purification afforded the title compound as a white solid (116 mg, 0.385 mmol, 77% yield).

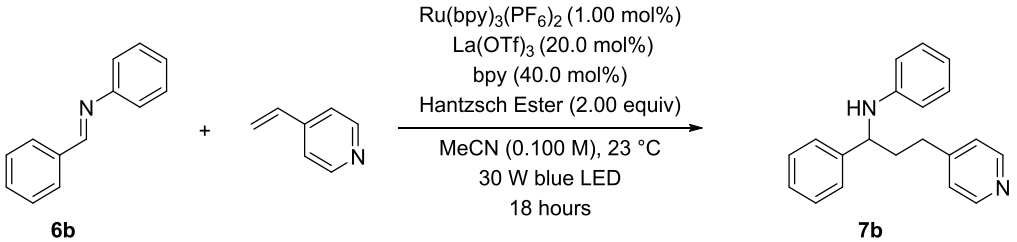
$\mathbf{R}_f$ = 0.35 (hexanes:EtOAc 2:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.51–8.47 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.12–7.07 (m, 4H), 6.67–6.63 (m, 1H), 6.51 (d, *J* = 8.2 Hz, 2H), 4.33–4.29 (m, 1H), 4.03 (br. s, 1H), 2.75–2.64 (m, 2 H), 2.33 (s, 3H), 2.20–2.13 (m, 1H), 2.13–2.05 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 150.9, 149.7, 147.2, 140.2, 137.0, 129.6, 129.3, 126.4, 124.0, 117.6, 113.4, 57.3, 38.9, 32.1, 21.2.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{21}H_{23}N_2$ ($[M + H]^+$): 303.1856, found: 303.1860.

***N*-(1-Phenyl-3-(pyridin-4-yl)propyl)aniline (7b)**




**6b** 2.0 equiv | 1.0 equiv | **7b** 72%

In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (*E*)-*N*,1-Diphenylmethanimine (**6b**) (181 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 μL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 3:2 (v/v). The purification afforded the title compound as a slightly yellow solid (104 mg, 0.359 mmol, 72% yield).

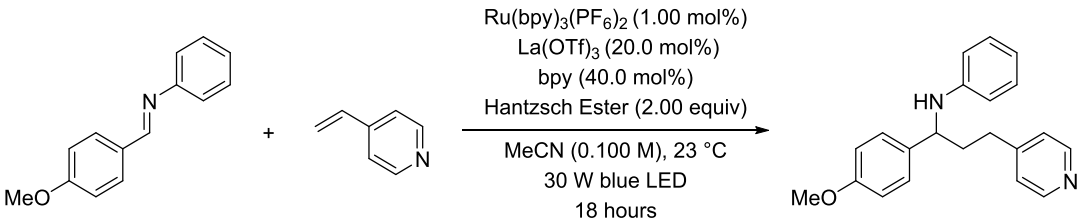
**$R_f$** = 0.47 (hexanes:EtOAc 1:1 (v/v)).

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 8.52–8.47 (m, 2H), 7.36–7.29 (m, 4H), 7.26–7.22 (m, 1H), 7.14–7.05 (m, 4H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.9 Hz, 2H), 4.34 (t, *J* = 6.9 Hz, 1H), 4.04 (br. s, 1H), 2.79–2.64 (m, 2H), 2.22–2.06 (m, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 150.7, 149.7, 147.1, 143.3, 129.2, 128.8, 127.3, 126.4, 124.0, 117.5, 113.4, 57.5, 38.9, 32.0.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{21}N_2$ ($[M + H]^+$): 289.1699, found: 289.1704.

***N*-(1-(4-Methoxyphenyl)-3-(pyridin-4-yl)propyl)aniline (7c)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (*E*)-1-(4-Methoxyphenyl)-*N*-phenylmethanimine (**6c**) (211 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 µL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 µmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 3:2 (v/v). The purification afforded the title compound as a yellow solid (126.3 mg, 0.397 mmol, 79% yield).

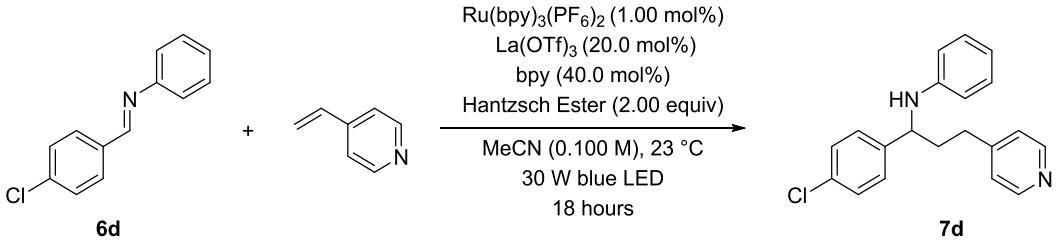
$\mathbf{R_f}$ = 0.36 (hexanes:EtOAc 2:3 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.50 (d, *J* = 4.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.14–7.06 (m, 4H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.70–6.64 (m, 1H), 6.52 (d, *J* = 8.2 Hz, 2 H), 4.30 (t, *J* = 7.8 Hz, 1H), 4.06 (br. s, 1H), 3.79 (s, 3H), 2.76–2.62 (m, 2 H), 2.21–2.12 (m, 1H), 2.12–2.03 (m, 1H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 158.8, 150.8, 149.7, 147.2, 135.2, 129.2, 127.5, 124.0, 117.5, 114.2, 113.4, 56.9, 55.3, 38.9, 32.0.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{21}H_{23}N_2O$ ($[M + H]^+$): 319.1805, found: 319.1793.

***N*-(1-(4-Chlorophenyl)-3-(pyridin-4-yl)propyl)aniline (7d)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s

to 1 min). (*E*)-1-(4-Chlorophenyl)-*N*-phenylmethanimine (**6d**) (216 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 μL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 3:2 (v/v). The purification afforded the title compound as a yellow solid (86.4 mg, 0.268 mmol, 54% yield).

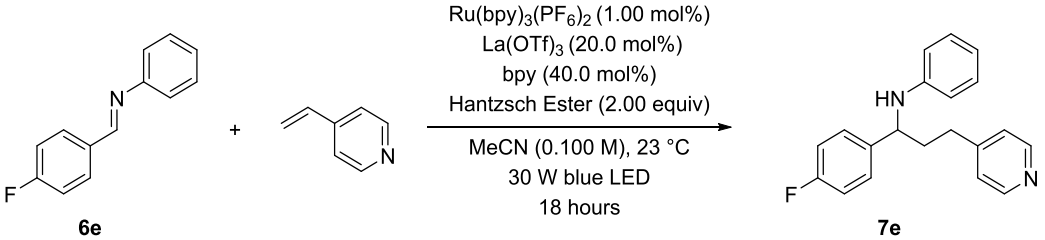
$\mathbf{R}_f$ = 0.32 (hexanes:EtOAc 1:1 (v/v)).

**$^1$H NMR** (700 MHz, $CDCl_3$, δ): 8.51 (d, *J* = 5.6 Hz, 2H), 7.36–7.23 (m, 4H), 7.15–7.05 (m, 4H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 4.33 (t, *J* = 6.78 Hz, 1H), 4.18 (br. s, 1H), 2.78–2.63 (m, 2H), 2.19–2.02 (m, 2H).

**$^{13}$C NMR** (176 MHz, $CDCl_3$, δ): 150.3, 149.8, 146.8, 142.0, 132.9, 129.3, 128.9, 127.8, 123.9, 117.8, 113.4, 56.9, 38.9, 31.9.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{20}ClN_2$ ($[M + H]^+$): 323.131, found: 323.1313.

***N*-(1-(4-Fluorophenyl)-3-(pyridin-4-yl)propyl)aniline (7e)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (*E*)-1-(4-Fluorophenyl)-*N*-phenylmethanimine (**6e**) (199 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 μL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 3:2 (v/v). The purification afforded the title compound as a yellow oil (114.9 mg, 0.375 mmol, 75% yield).

$\mathbf{R}_f$ = 0.28 (hexanes:EtOAc 1:1 (v/v)).

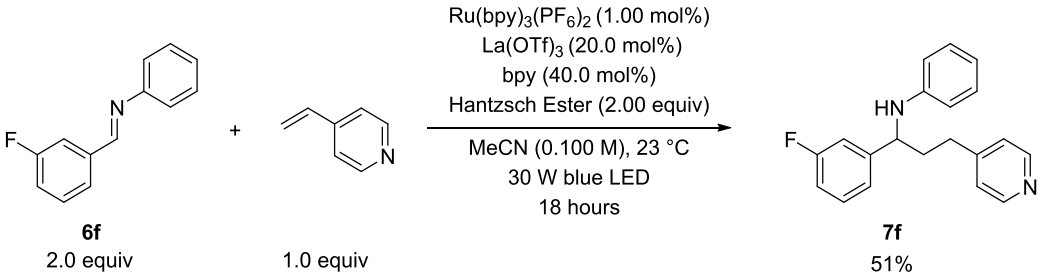
**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 8.50 (d, *J* = 5.8 Hz, 2H), 7.33–7.26 (m, 2H), 7.15–7.05 (m, 4H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 4.33 (t, *J* = 6.9 Hz, 1H), 4.28 (br. s, 1H), 2.77–2.63 (m, 2H), 2.20–2.02 (m, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 162.0 (d, *J* = 243.9 Hz), 150.7, 149.6, 146.9, 139.0 (d, *J* = 2.6 Hz), 129.3, 127.9 (d, *J* = 7.9 Hz), 124.0, 117.7, 115.6 (d, *J* = 21.4 Hz), 113.4, 56.9, 39.0, 32.0.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –116.0.

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{20}FN_2$ ($[M + H]^+$): 307.1605, found: 307.1609.

***N*-(1-(3-Fluorophenyl)-3-(pyridin-4-yl)propyl)aniline (7f)**




In a glovebox, an oven-dried 20 mL vial was charged with $La(OTf)_3$ (58.6 mg, 0.100 mmol, 20.0 mol%) and bipyridine (31.2 mg, 0.200 mmol, 40.0 mol%). MeCN (5.00 mL, 0.100 M, with respect to 4-vinylpyridine) was added and the mixture was stirred at 23 °C until the solution became homogeneous (30 s to 1 min). (*E*)-1-(3-Fluorophenyl)-*N*-phenylmethanimine (**6f**) (199 mg, 1.00 mmol, 2.00 equiv), 4-vinylpyridine (53.9 μL, 52.6 mg, 0.500 mmol, 2.00 equiv), Hantzsch Ester (253 mg, 1.00 mmol, 2.00 equiv), and $Ru(bpy)_3(PF_6)_2$ (4.30 mg, 5.00 μmol, 1.00 mol%) were then added. The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. 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 to 7:3 (v/v). The purification afforded the title compound as a yellow oil (78.8 mg, 0.257 mmol, 51% yield).

**$R_f$** = 0.28 (hexanes:EtOAc 1:1 (v/v)).

**$^1$H NMR** (500 MHz, $CDCl_3$, δ): 8.53–8.46 (m, 2H), 7.33–7.22 (m, 1H), 7.15–7.01 (m, 6H), 6.97–6.89 (m, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 2H), 4.34 (t, *J* = 6.8 Hz, 1H), 4.17 (br. s, 1H), 2.79–2.63 (m, 2H), 2.19–2.03 (m, 2H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$, δ): 163.3 (d, *J* = 245.0 Hz), 150.3, 149.9, 146.8, 146.4 (d, *J* = 6.3 Hz), 130.3 (d, *J* = 8.0 Hz), 129.3, 123.9, 122.1 (d, *J* = 2.5 Hz), 117.8, 114.3 (d, *J* = 21.4 Hz), 113.4, 113.2 (d, *J* = 21.6 Hz), 57.1, 38.9, 32.0.

**$^{19}$F NMR** (376 MHz, $CDCl_3$, 25 ºC, δ): –113.1 (s).

**HRMS** (ESI-TOF) (m/z): calcd for $C_{20}H_{20}FN_2$ ($[M + H]^+$): 307.1605, found: 307.1608.

# Mechanistic Studies

## The Luminescence Quenching Experiments

Emission intensities were recorded using a Perkin Elmer LS50B Luminescence spectrometer. All quenching data was recorded using a 1.00 cm screw-top quartz cuvette at 23 °C. The measurements were performed using a 2.5 μM solution of $Ru(bpy)_3(PF_6)_2$ in degassed MeCN with varying concentration of a quencher. The samples were excited at 452 nm and emission intensity was recorded at 615 nm.

Stern-Volmer experiment indicated that Hantzsch ester (HEH, $E_{1/2}^{red}$ = +0.887 V vs SCE) does not quench the luminescence of $*Ru(bpy)^{2+}$ ($E_{1/2}^{red}$ = +0.77 V vs SCE) in MeCN (**Figure S3**). This result is in agreement with Kellogg's observation where *N*-methylated Hantzsch ester (Me-HE, $E_{1/2}^{red}$ = + 0.878 V vs SCE) does not quench $*Ru(bpy)^{2+}$.[5]

***NOTE:*** We could not conduct the quenching experiment using a higher concentration of HEH due to its poor solubility in MeCN.

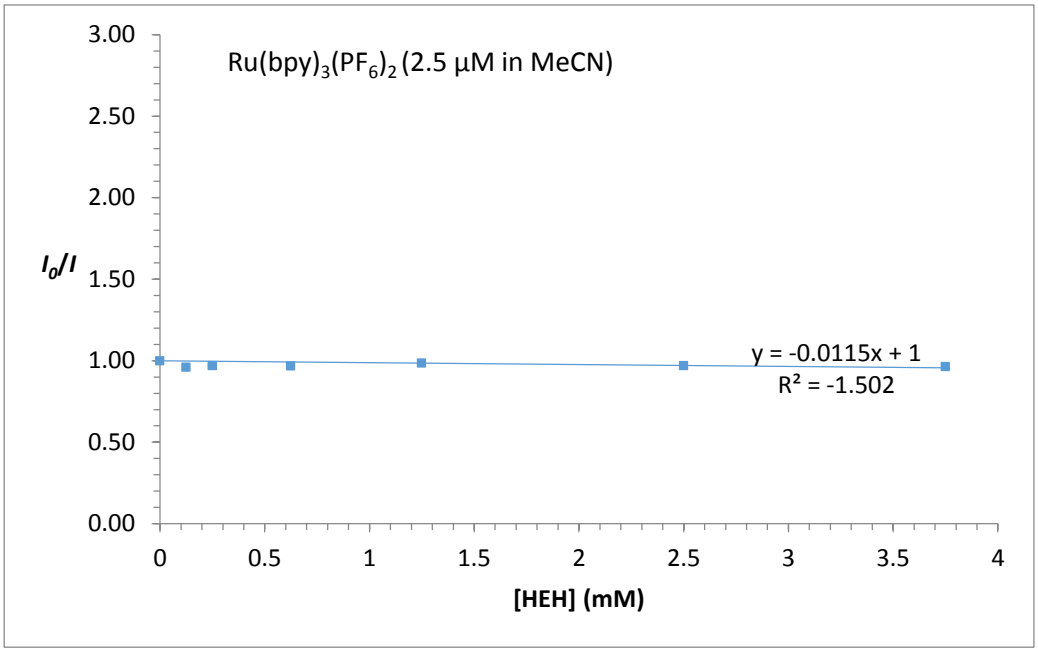



**Figure S3.** $*Ru(bpy)_3(PF_6)_2$ Emission Quenching by Hantzsch Ester in MeCN.

We also ran the luminescence quenching experiment of *Ru(bpy)$^{2+}$ in DMF (**Figure S4**) since similar studies were previously reported.[6] However, as in the case of MeCN, we did not see any significant quenching.

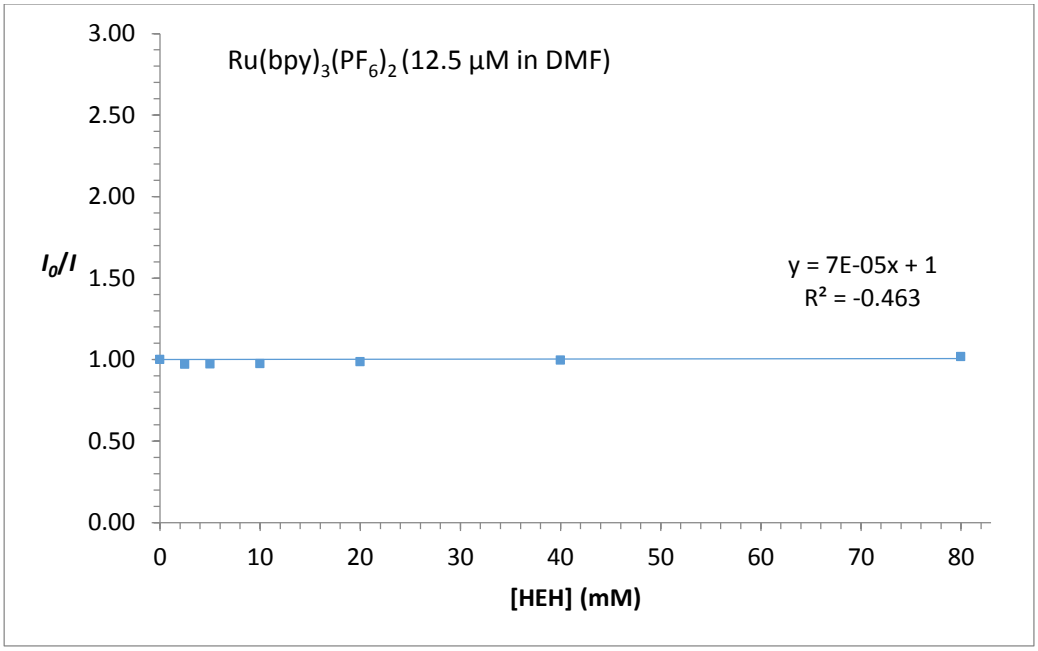



**Figure S4.** *$Ru(bpy)_3(PF_6)_2$ Emission Quenching by Hantzsch Ester in DMF.

In addition, neither 4-vinylpyridinde (**Figure S5**), nor benzaldehyde (**Figure S6**) quenched the luminescence of *Ru(bpy)$^{2+}$ in MeCN.

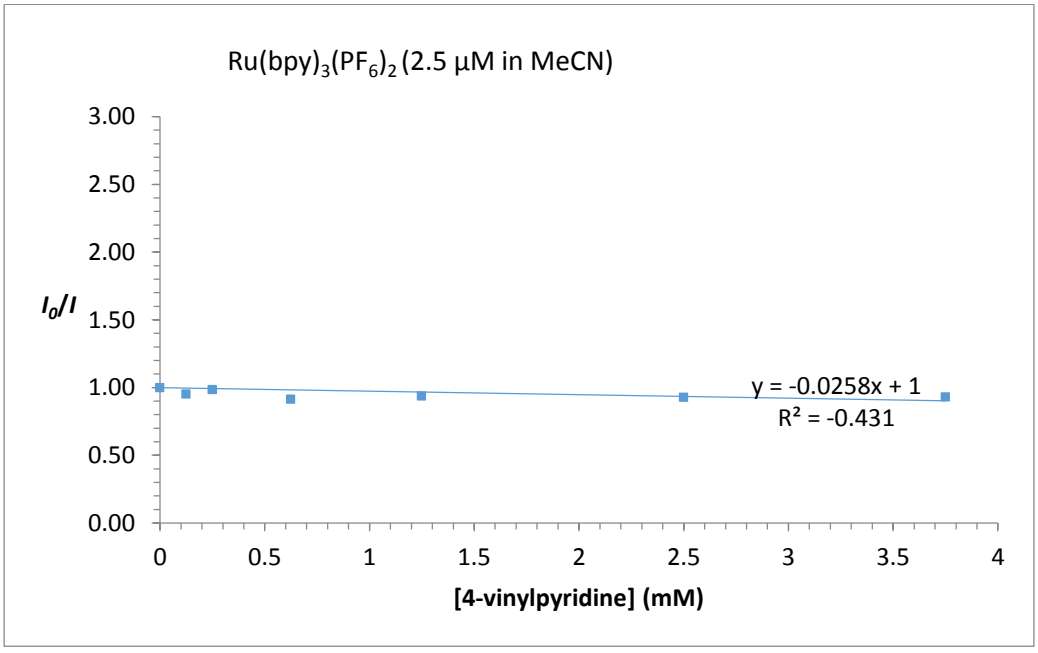



**Figure S5.** *$Ru(bpy)_3(PF_6)_2$ Emission Quenching by 4-vinylpyridine in MeCN.

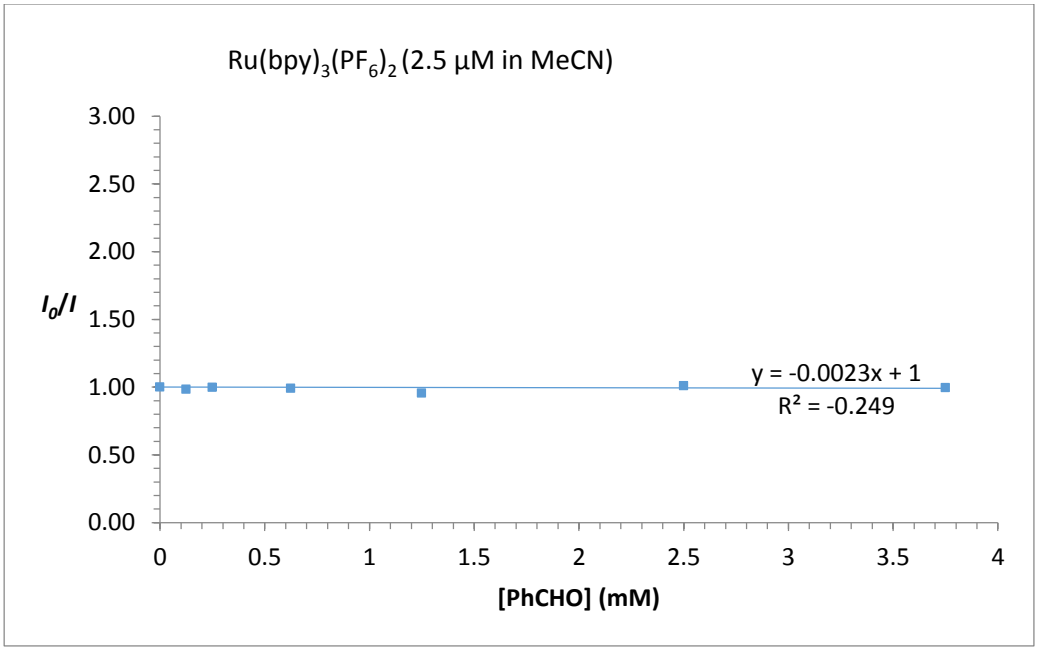



**Figure S6.** *$Ru(bpy)_3(PF_6)_2$ Emission Quenching by PhCHO in MeCN.

We also performed Stern-Volmer experiments using the following compounds or combinations of compounds as potential quenchers of *$Ru(bpy)_3^{2+}$ (i) benzaldehyde + $La(OTf)_3$ + bpy; (ii) 4-vinylpyridne + $La(OTf)_3$ + bpy; (iii) benzaldehyde + HEH; (iv) 4-vinylpyridne + HEH; (v) benzaldehyde + 4-vinylpyridne + HEH + $La(OTf)_3$ + bpy. None of the above experiments showed quenching of luminescence generated by *$Ru(bpy)_3^{2+}$. Since none of the reaction components have any effect on the luminescence of *$Ru(bpy)_3^{2+}$, we hypothesized that *$Ru(bpy)_3^{2+}$ is quenched either by the photoexcited Hanztsch ester, or by a catalytically generated intermediate that is not present at the start of the reaction, most likely Hantzsch ester radical (HEH•).[7]

## Pinacol Coupling Reaction

We observed that pinacol coupling reaction takes place in the absence of $Ru(bpy)_3(PF_6)_2$ and the Lewis acid (**Figure S7a**), thus indicating that binding between aldehydes and $La^{3+}$ is not required for the SET to take place. In addition, when we performed a reaction with a laser line filter (CWL = 488 ± 2 nm, FWHM = 10 ± 2 nm), we did not observe pinacol coupling product. Since excitation of the HEH to *HEH is impossible at λ = 488 nm, we concluded that excited Hantzsch ester is needed for reaction to proceed. Furthermore, addition of $Ru(bpy)_3(PF_6)_2$ increased the product yield (**c**). This suggests that excited $Ru(bpy)_3(PF_6)_2$ is engaged in and facilitates the electron transfer process.

Experimental procedures: In a glovebox, to an oven-dried 4.0 mL vial charged with Hantzsch ester (5.80 mg, 0.0229 mmol, 1.00 equiv) and MeCN (0.115 mL, 0.200 M) was added 4-(trifluoromethyl)benzaldehyde (3.99 µL, 0.229 mmol, 1.00 equiv). The reaction vial was capped, taken out of the glovebox, and placed 30 mm from a blue LED light source (λ = 455 nm, 30 W). The reaction mixture was stirred for 18 hours at 23 °C while being irradiated with blue LED light. After that time, the reaction mixture was concentrated *in vacuo*. Methyl 4-methoxybenzoate (3.81 mg, 0.0229 mmol, 1.00 equiv) and

$CDCl_3$ (0.500 mL) were then added and the yield of the pinacol coupling reaction was determined by $^1H$ NMR.

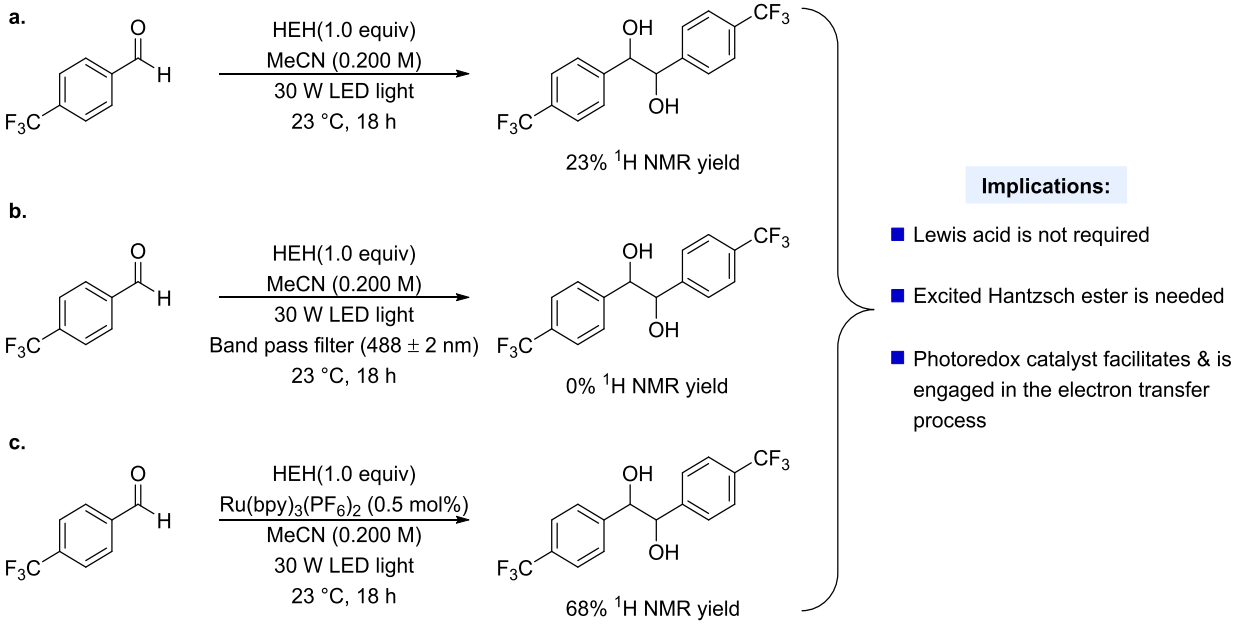



**Figure S7.** Pinacol coupling reaction performed with HEH upon blue light irradiation.

UV-Vis absorption spectrum showed that HEH has a maximum absorbance at λ = 362 nm in MeCN (**Figure S8**). The non-zero absorbance at λ = 410-420 nm indicates that HEH can absorb the light emitted by our blue LED (**Figure S9**), undergoing photoexcitation to its excited state, *HEH. Excited Hantzsch ester, *HEH, can then engage in an SET process with the aldehyde, generating a ketyl radical (single electron reduction of carbonyl groups with HEH to afford intermediate ketyl radicals has been previously reported).[8]

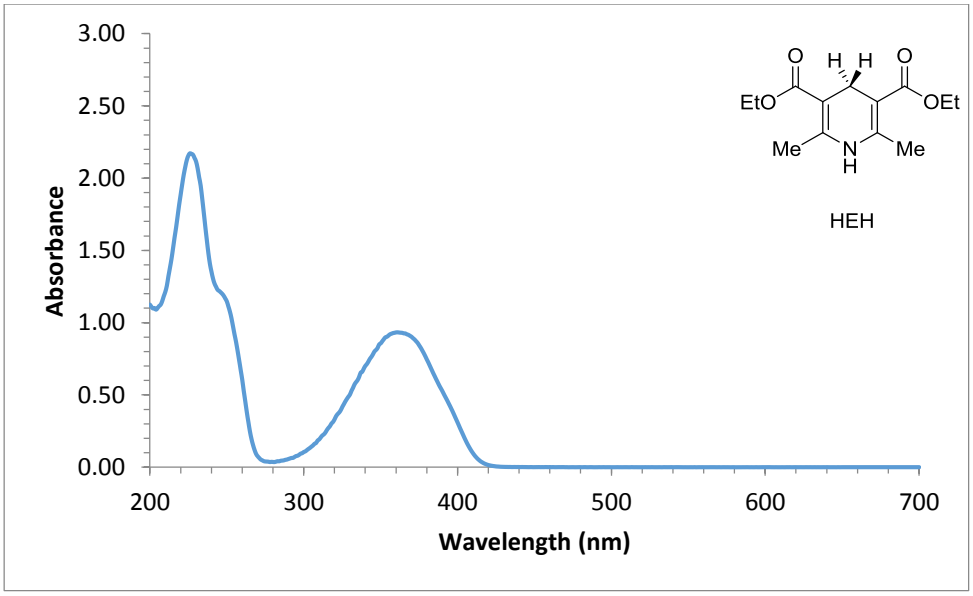



**Figure S8.** UV-Vis of Hantzsch ester in MeCN.

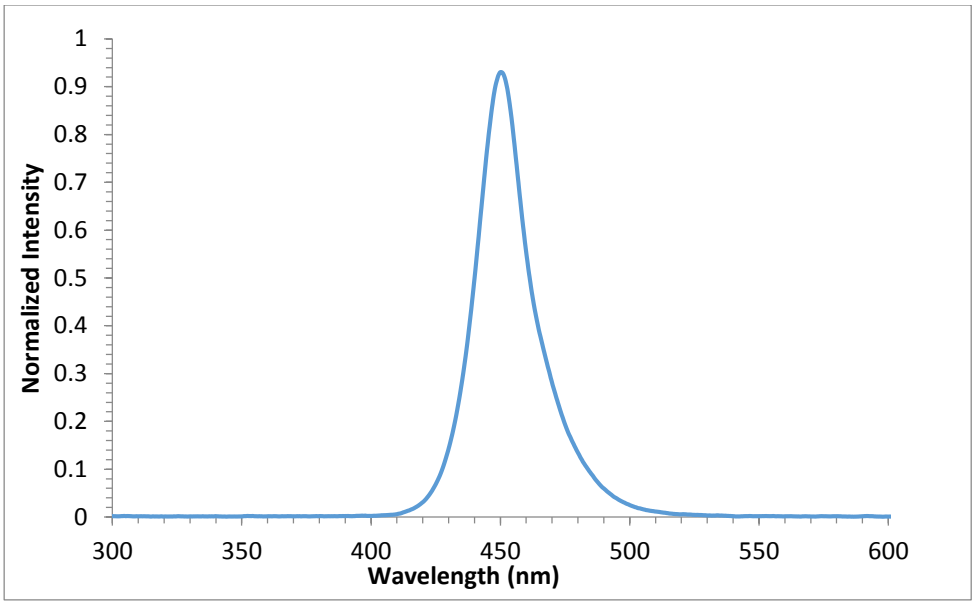



**Figure S9.** Emission spectrum of the 30 W LED light.

In order to investigate whether *HEH is the quencher of *$Ru(bpy)_3^{2+}$, we performed a reaction with a laser line filter (CWL = 488 ± 2 nm, FWHM = 10 ± 2 nm, **Figure S10**). Since excitation of the HEH to *HEH is nearly impossible at λ = 488 nm, and the reaction still proceeds in a good yield with the filter, we concluded that excitation of Hantzsch ester is not necessary to propagate the photocatalytic cycle. Based on this experiment and the quenching data, HEH• is the most likely quencher of *$Ru(bpy)_3^{2+}$. Initial amount of HEH• required to initiate the catalytic cycle is generated by photoexcitation of HEH, followed by a SET from *HEH to an aldehyde, as in the pinacol coupling reaction in the absence of a $Ru(bpy)_3(PF_6)_2$.

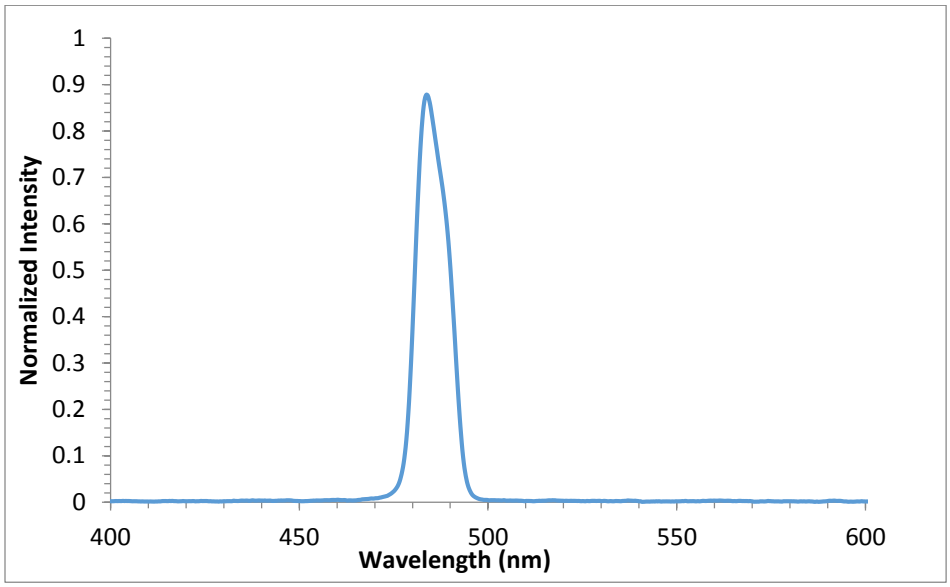



**Figure S10.** Emission spectrum of the LED light with the laser line filter *(CWL = 488 nm)*.

## Study of Substrates and Lewis Acid Interaction by $^1$H NMR in MeCN-$d_3$

All NMR samples were prepared in a glovebox under nitrogen atmosphere using screw-cap NMR test tubes and MeCN-$d_3$ (0.75 mL) as the solvent. NMR spectra were recorded on a Bruker Ascend 700 spectrometer operating at 700 MHz for $^1$H acquisitions (**Figure S11**).

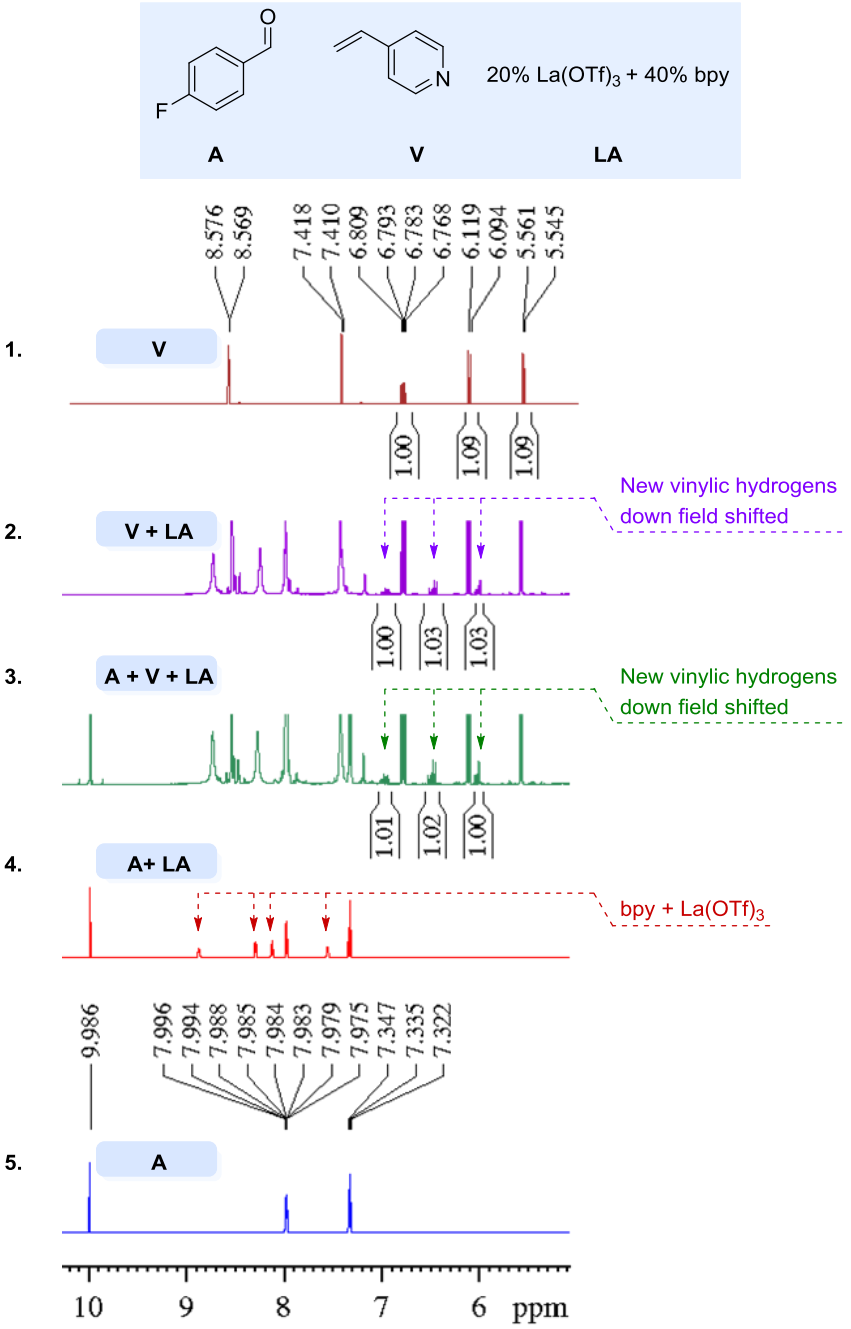



**Figure S11. Studies of substrates and Lewis acid interaction by $^1$H NMR in MeCN-$d_3$.**

**Spectrum 1:** Vinylpyridine (0.075 mmol) in MeCN-$d_3$ (0.75 mL)

**Spectrum 2**: $La(OTf)_3$ (0.015 mmol) and bpy (0.030 mmol) were mixed and stirred in MeCN-$d_3$ (0.75 mL) for 1 minute forming a clear solution, then to the solution was added vinylpyridine (0.075 mmol). 10% new products (with vinylic protons shifted downfield) were formed, indicating the vinylpyridine is coordinated with the Lewis acid complex.

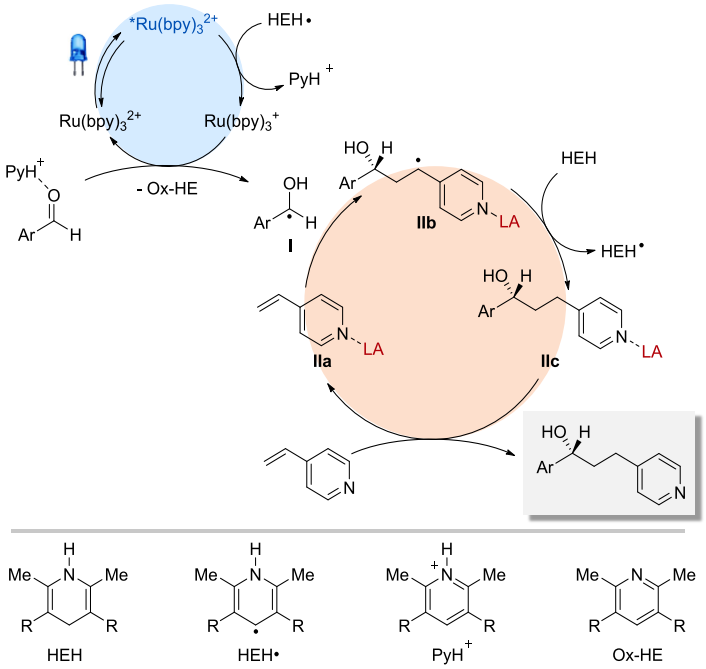
**Spectrum 3:** $La(OTf)_3$ (0.015 mmol) and bpy (0.030 mmol) were mixed and stirred in MeCN-$d_3$ (0.75 mL) for 1 minute forming a clear solution, then to the solution was added vinylpyridine (0.075 mmol) and 4-fluorobenzladehyde (0.075 mmol). 10% new products were formed and the products are the same as the one shown in spectrum 1, indicating the Lewis acid preferably binds to the vinylpyridine instead of the aldehyde.

**Spectrum 4:** $La(OTf)_3$ (0.015 mmol) and bpy (0.030 mmol) were mixed and stirred in MeCN-$d_3$ (0.75 mL) for 1 minute forming a clear solution, then to the solution was added 4-fluorobenzladehyde (0.075 mmol).

**Spectrum 5:** 4-fluorobenzaldehyde (0.075 mmol) in MeCN-$d_3$ (0.75 mL). Spectrum 4 and 5 indicate that aldehyde shows no change in chemical shift after mixing with the Lewis acid, therefore the aldehyde is unlikely bound to the Lewis acid.

## Summary of the mechanistic studies:

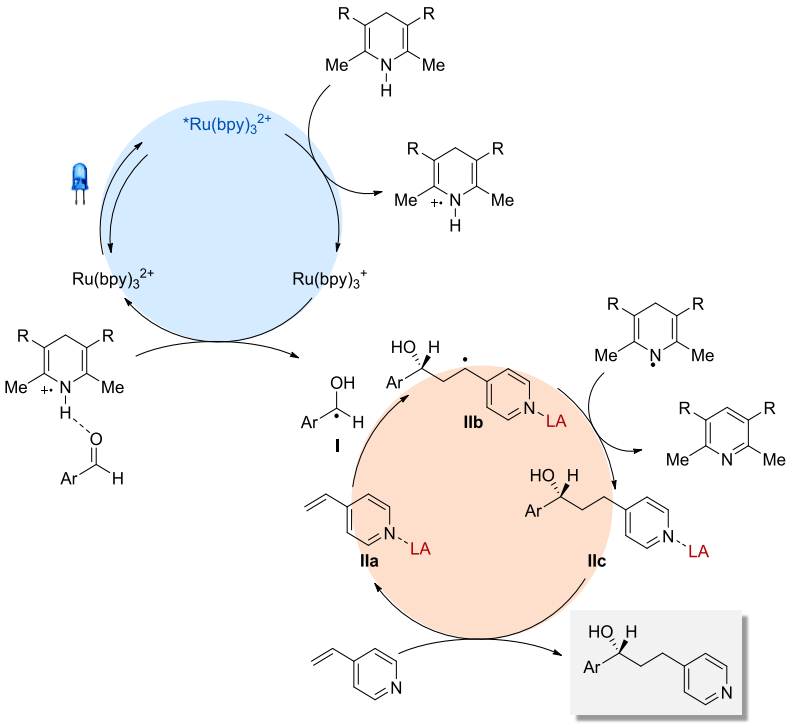
- The results of the Stern-Volmer experiments (**Figures S3-S6**) indicate that none of the reactions components or the combination thereof has any detectable effect on the luminesce intensity of $*Ru(bpy)_3^{2+}$. Thus, we have proposed that catalytically-generated HEH• is the most likely quencher of $*Ru(bpy)_3^{2+}$.[7]
- We observed that pinacol coupling reaction proceeds efficiently when a mixture of an aldehyde and Hantzsch ester in MeCN is irradiated with blue light (**Figure S7**). Based on this observation, we concluded the following: (i) HEH• can be readily formed at the beginning of the reaction upon a single-electron reduction of an aldehyde by *HEH; (ii) an additional Lewis acid additive is not required for the formation of a ketyl radical, so $La(OTf)_3$-bpy complex most likely plays a different role during the reaction.
- We postulated that $La(OTf)_3$-bpy activates 4-vinylpyridine and facilitates the ketyl radical addition process: (i) in the absence of $La(OTf)_3$-bpy the reaction yields a pinacol coupling product; (ii) upon addition of $La(OTf)_3$-bpy to 4-vinylpyridine, a change in chemical shift of 4-vinylpyridine's protons is observed (**Figure S11**).
- These observations lead to the proposed reaction mechanism shown in **Scheme S1**.




**Scheme S1.** Proposed reaction mechanism.

## An Alternative Reaction Mechanism

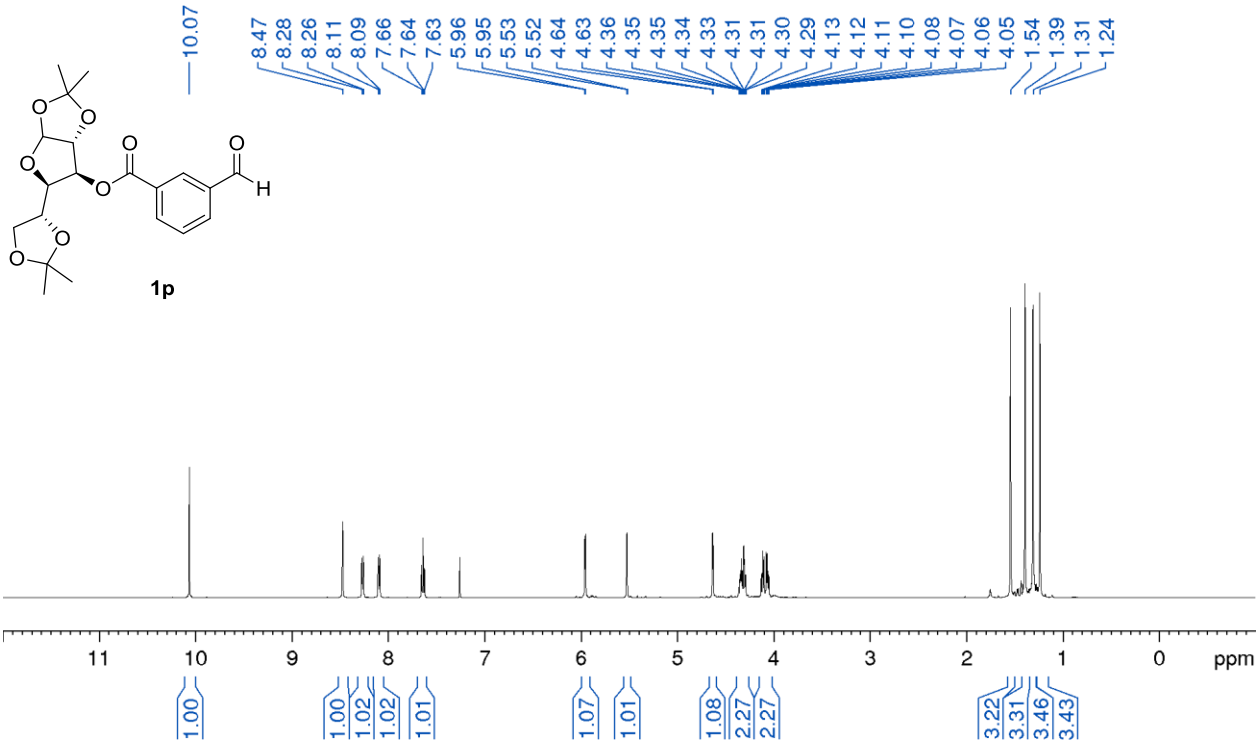
We also considered an alternative reaction pathway (**Scheme S2**), but it appears less likely based on the results of the Stern-Volmer quenching experiments.



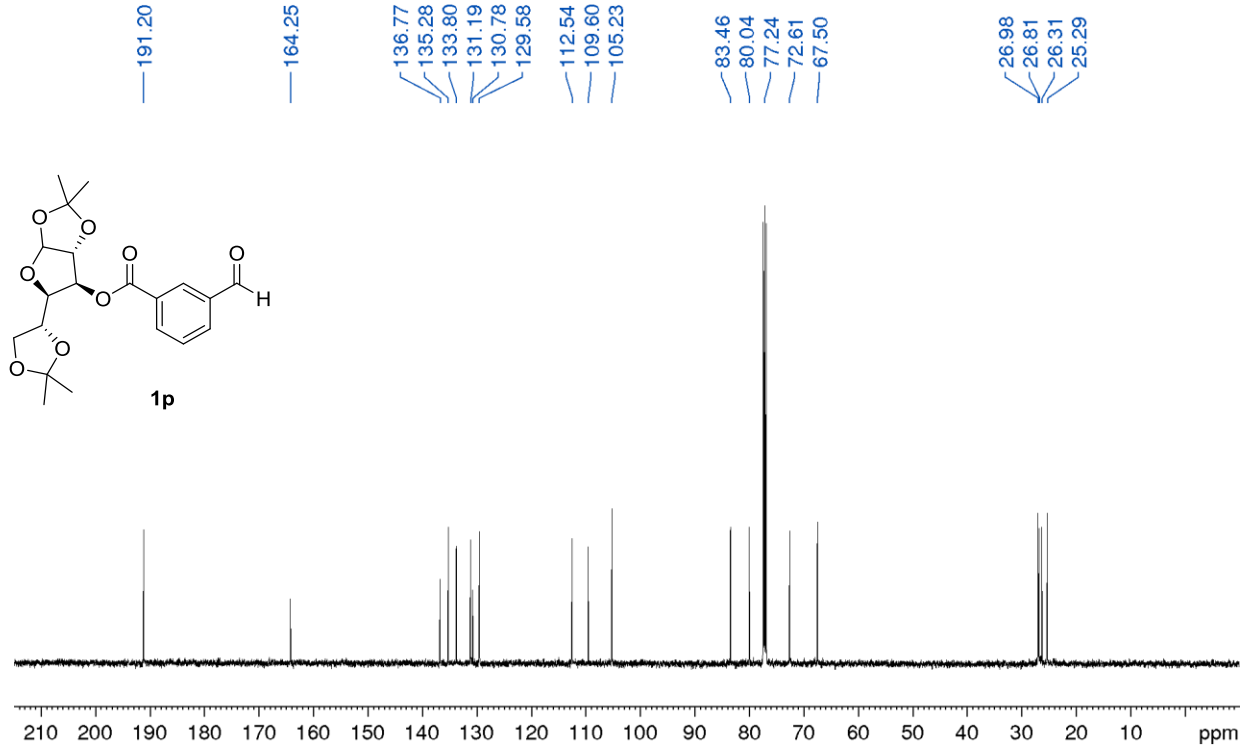

**Scheme S2.** An alternative reaction pathway.

# Spectroscopic Data

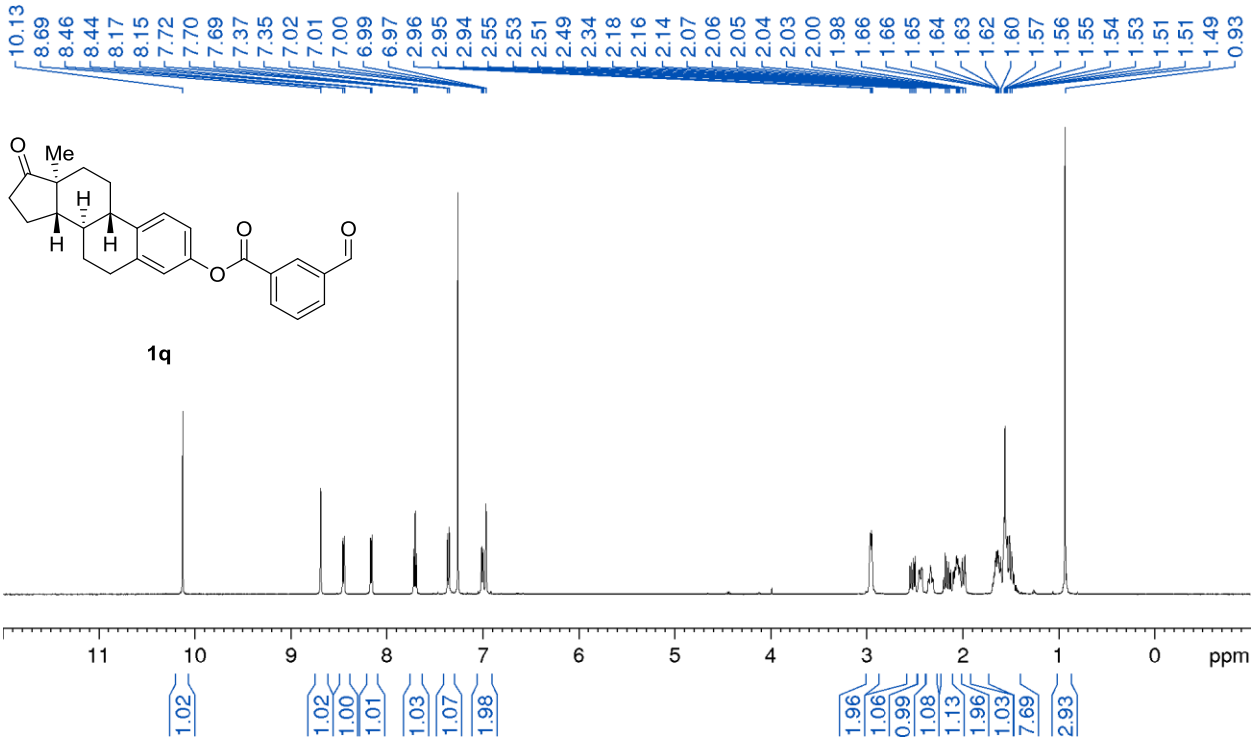
$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **1p**



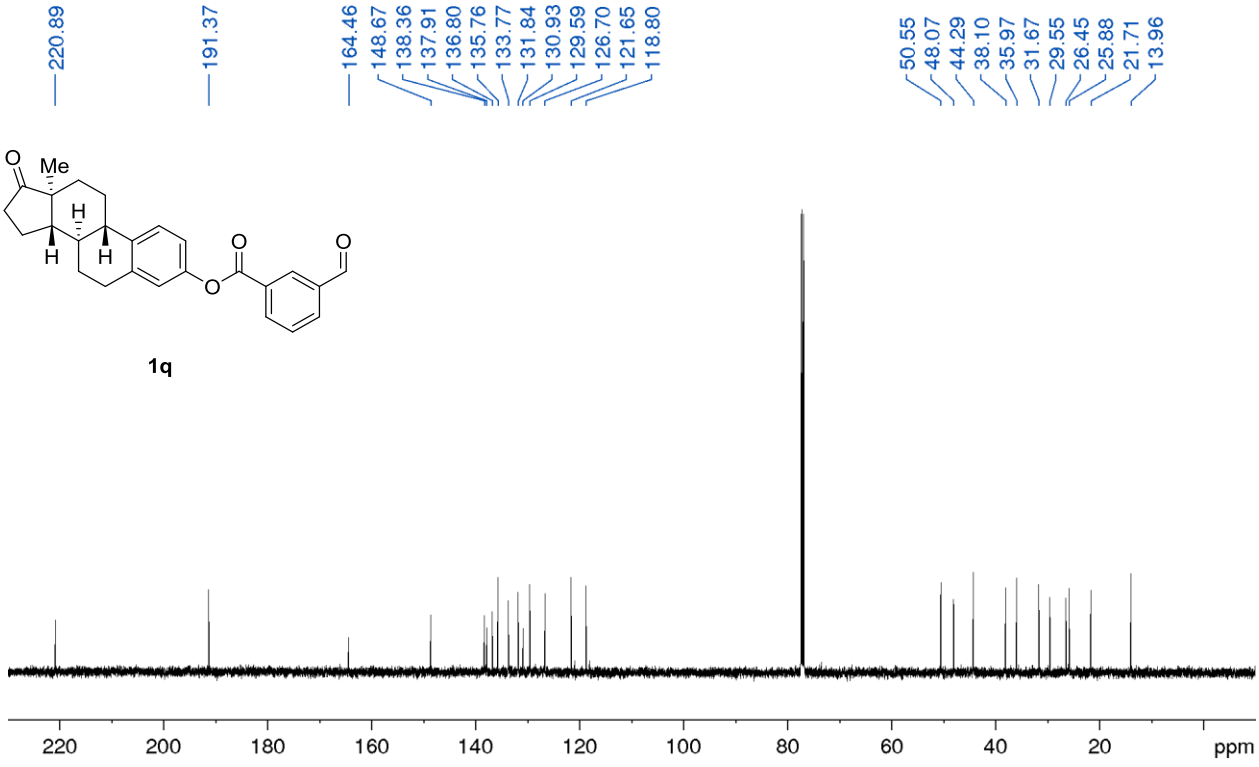

$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **1p**



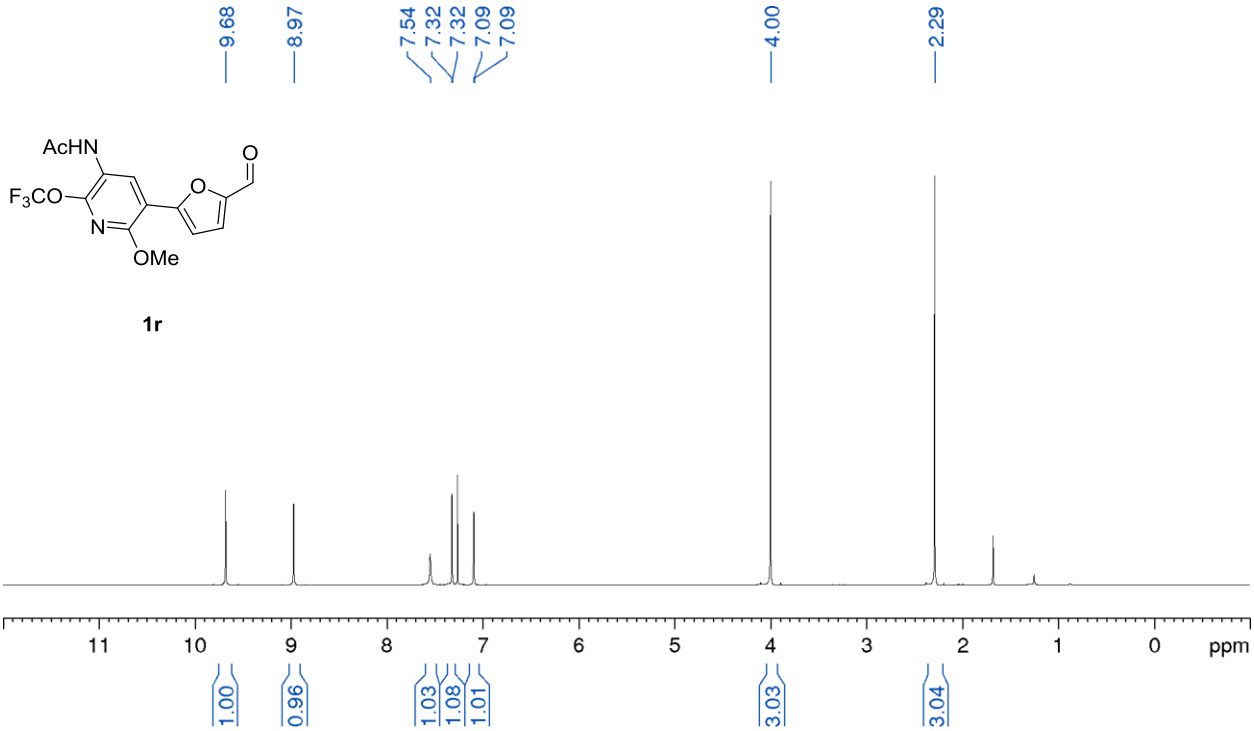
$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **1q**



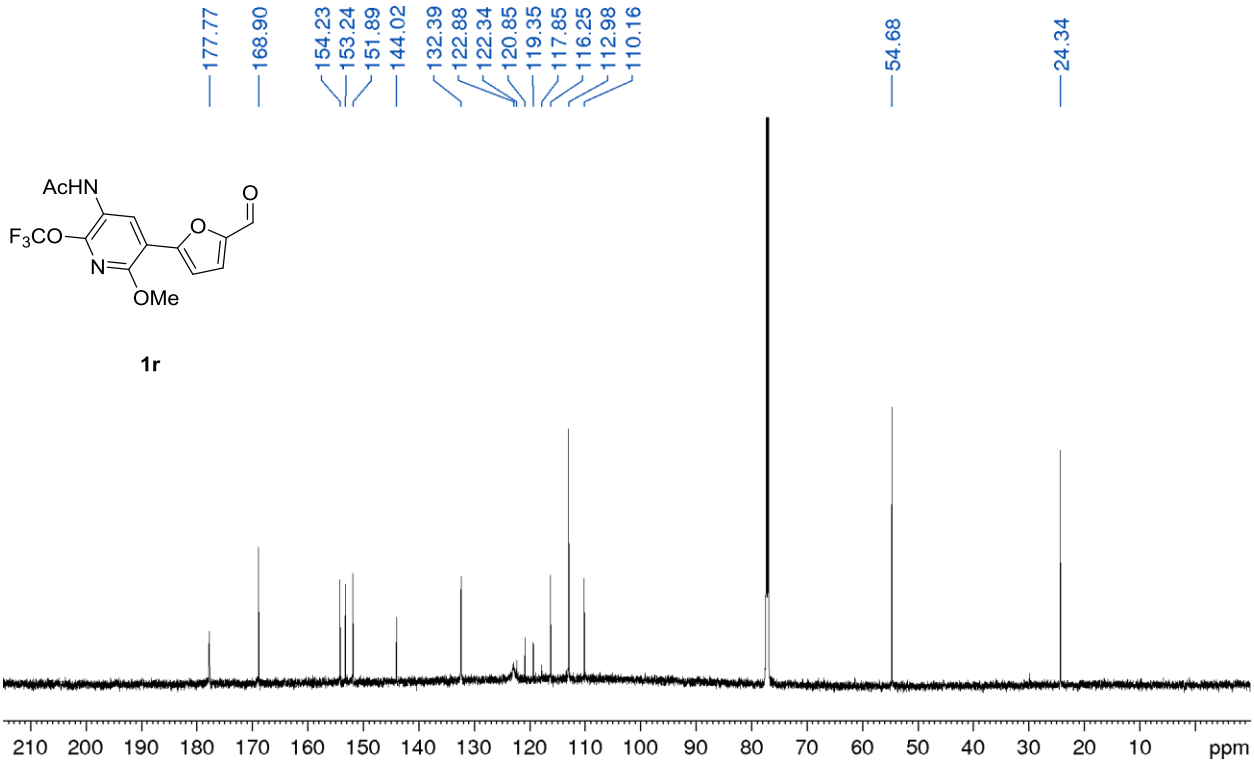

$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **1q**



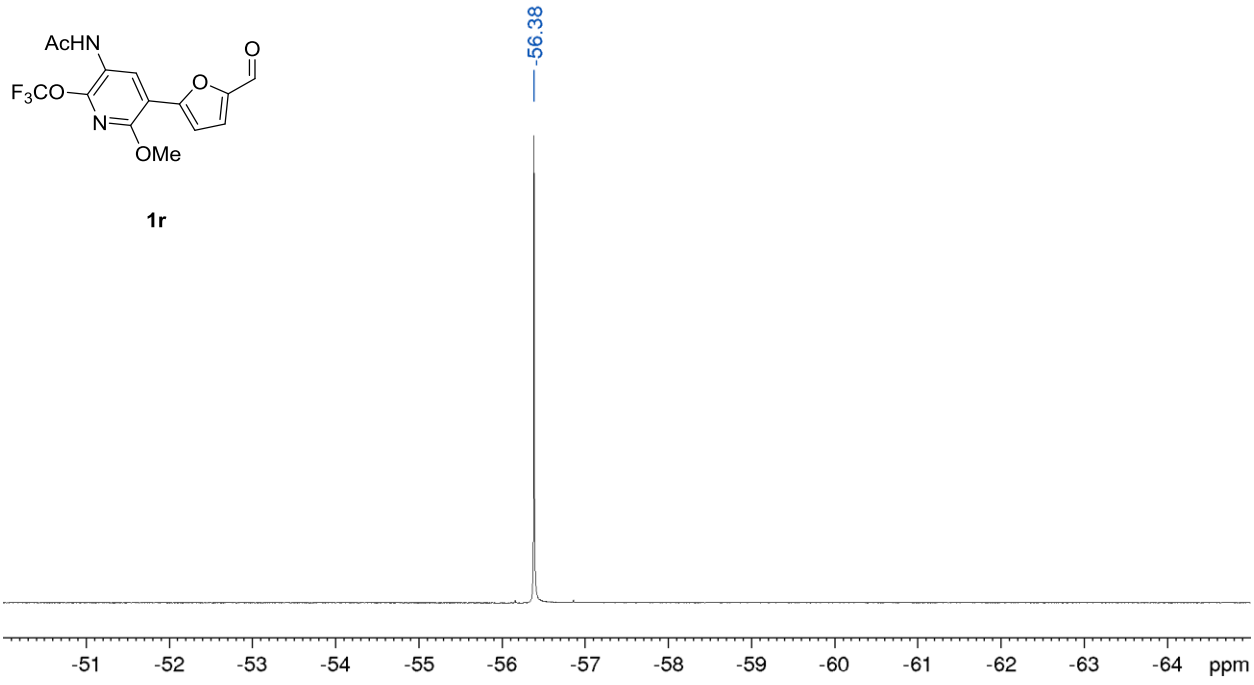
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **1r**



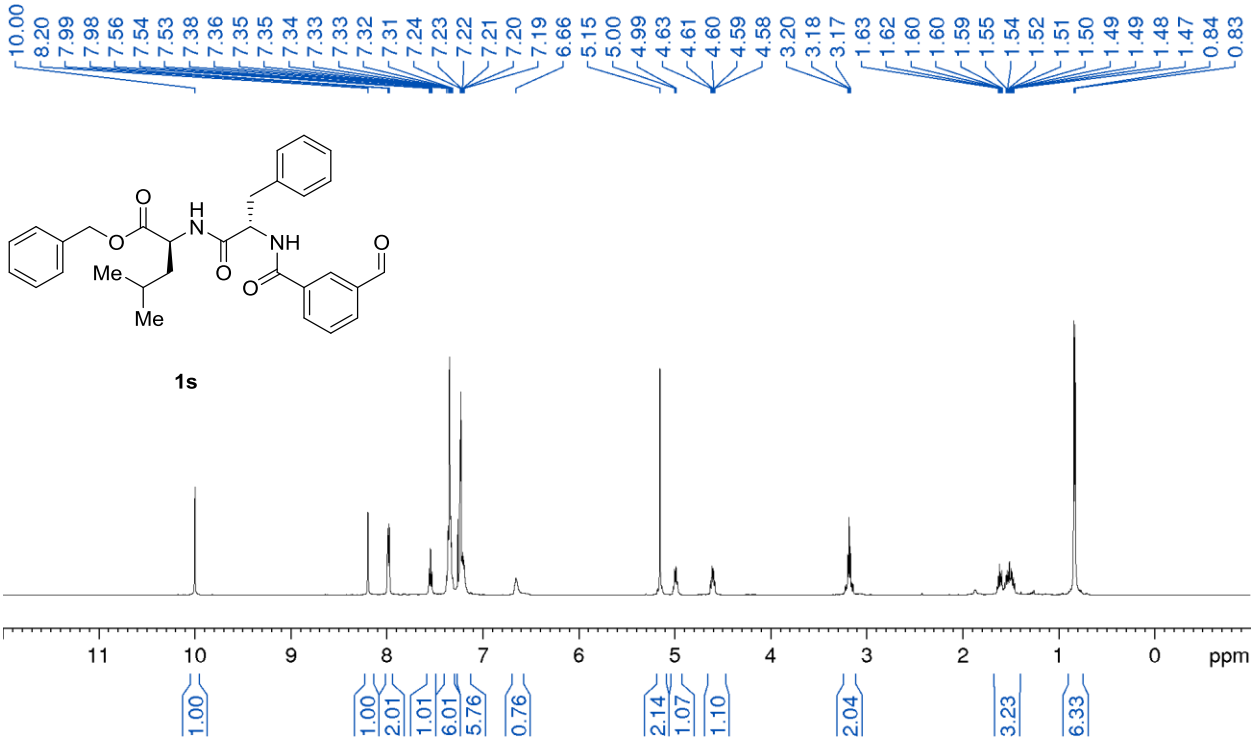

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **1r**



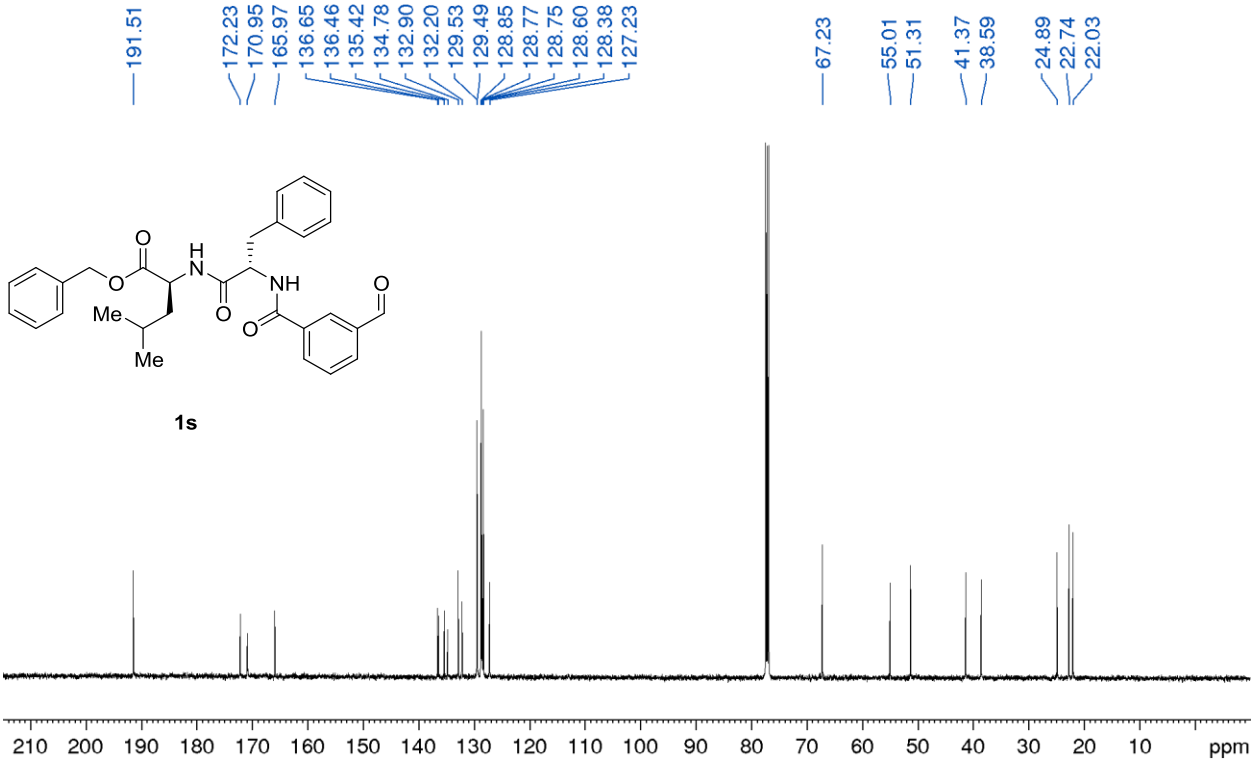
$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **1r**



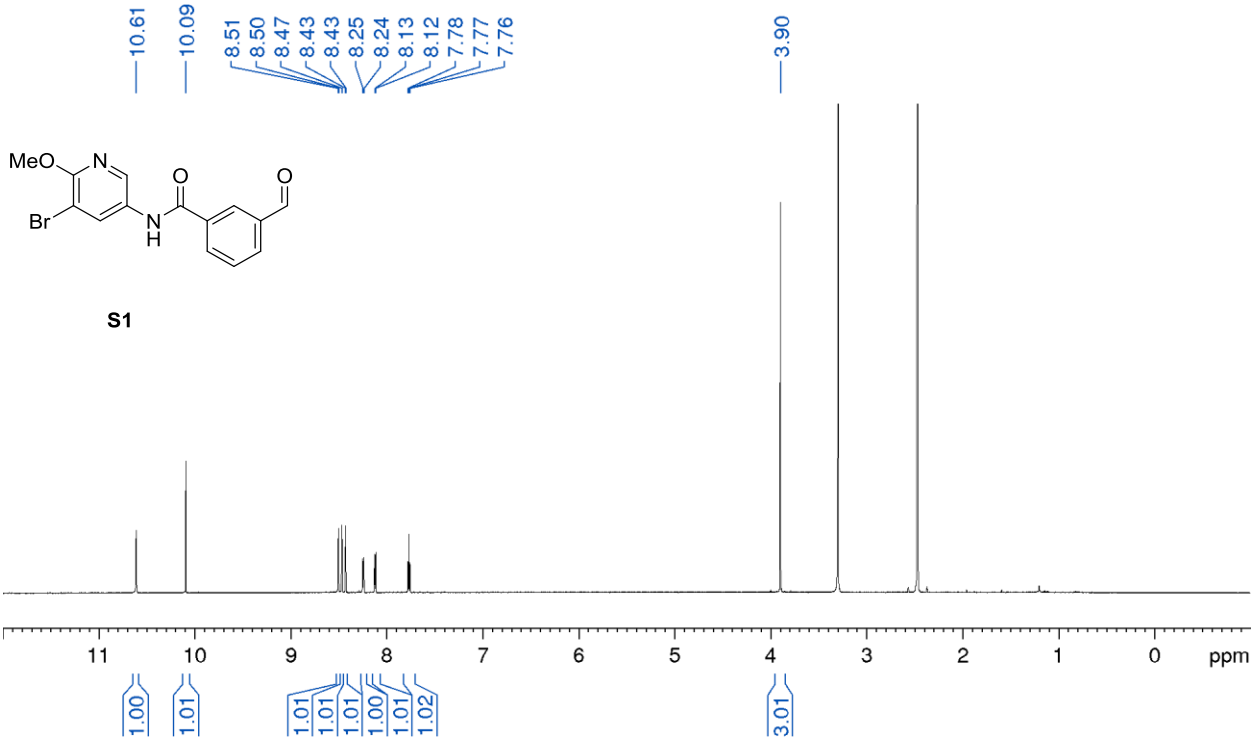

$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **1s**



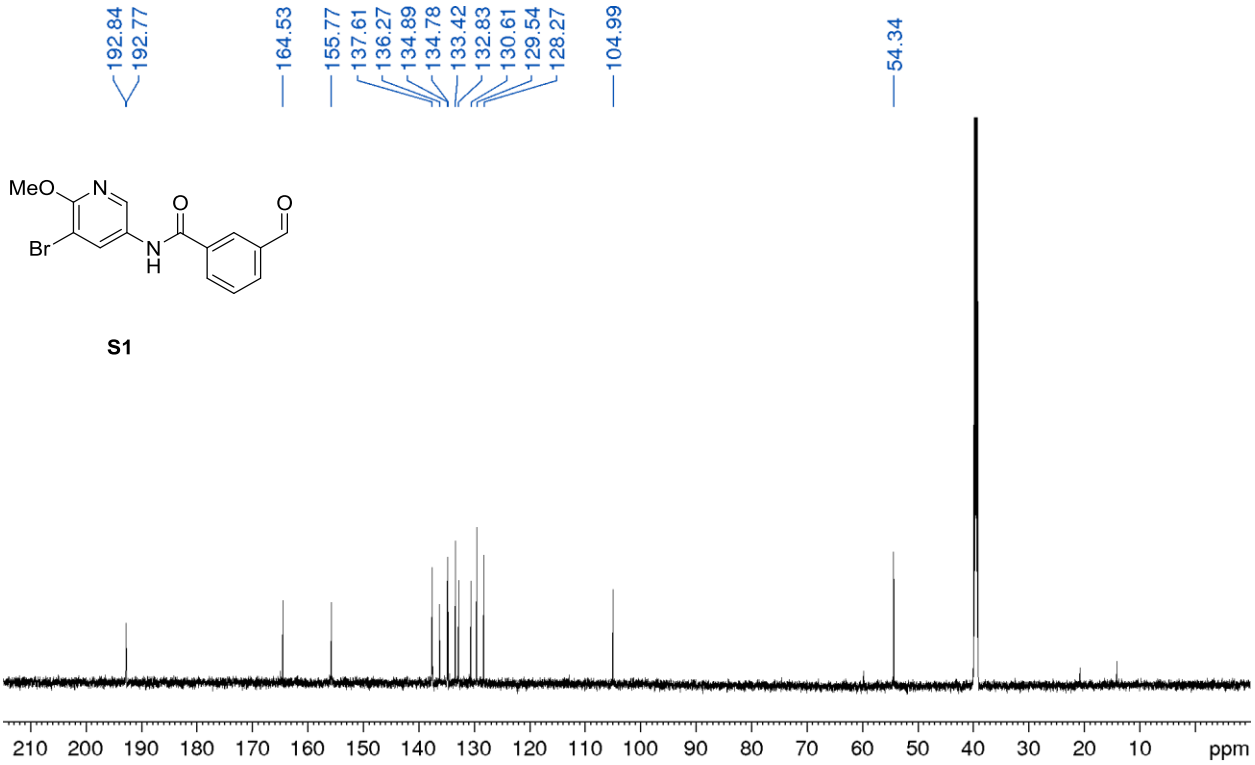
$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **1s**



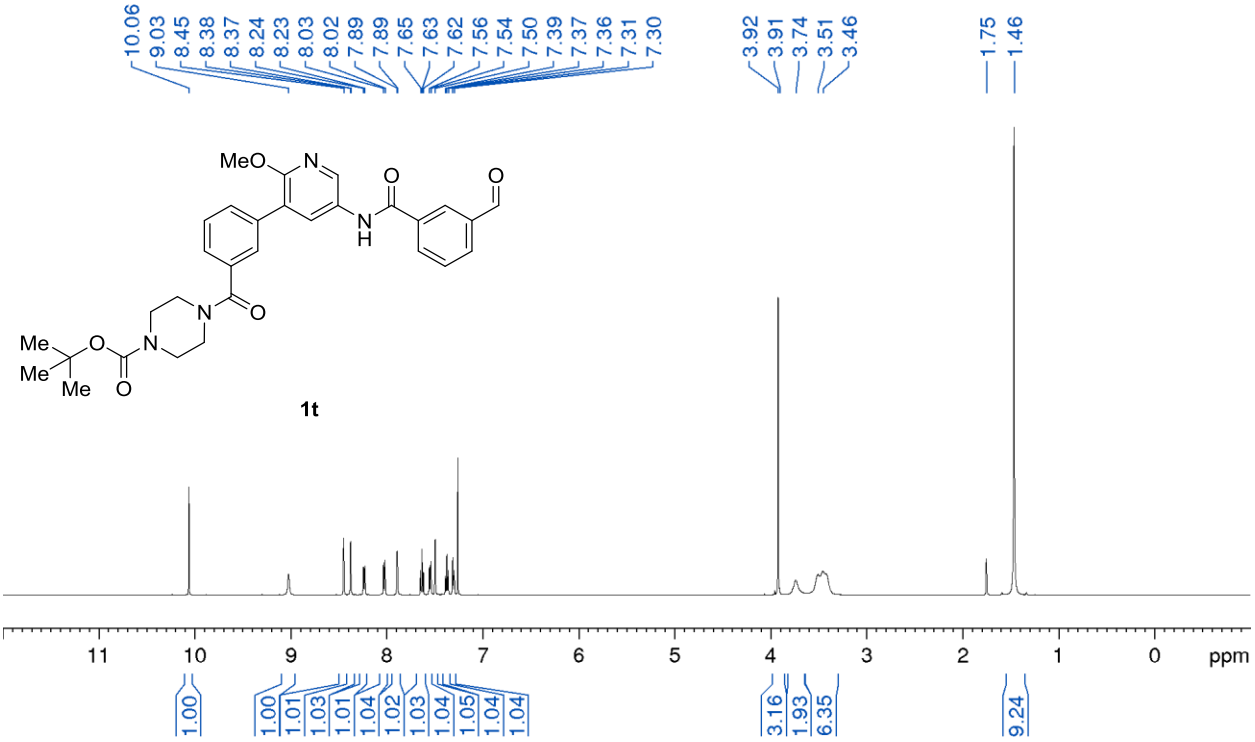

$^{1}$H NMR (700 MHz, $(CD_3)_2SO$, 25 ºC) of **S1**



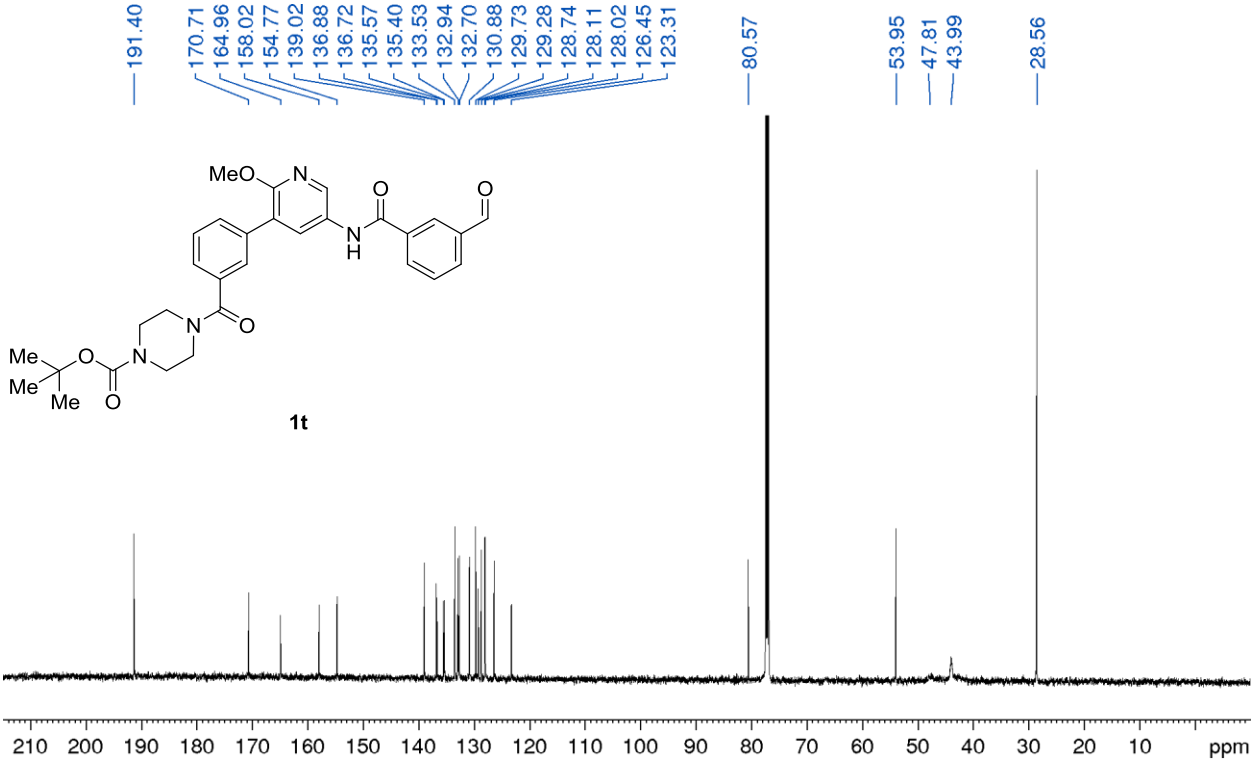
$^{13}$C NMR (176 MHz, $(CD_3)_2SO$, 25 ºC) of **S1**



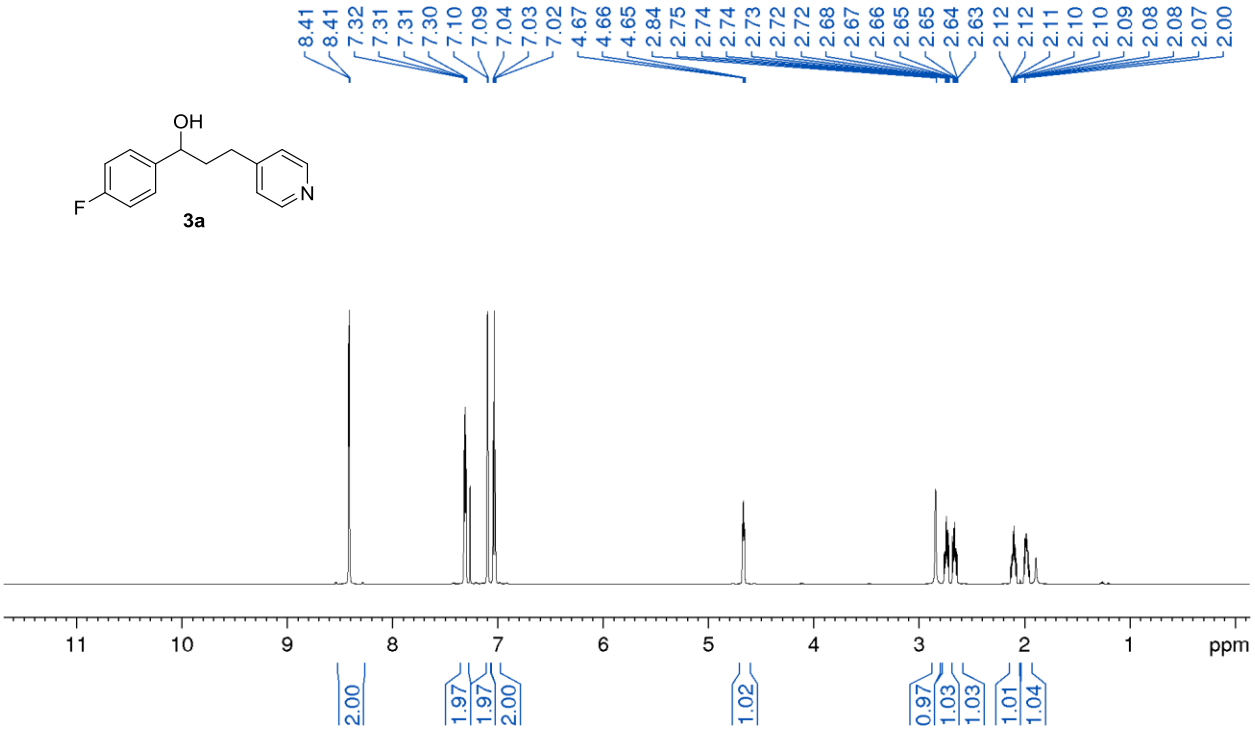

$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **1t**



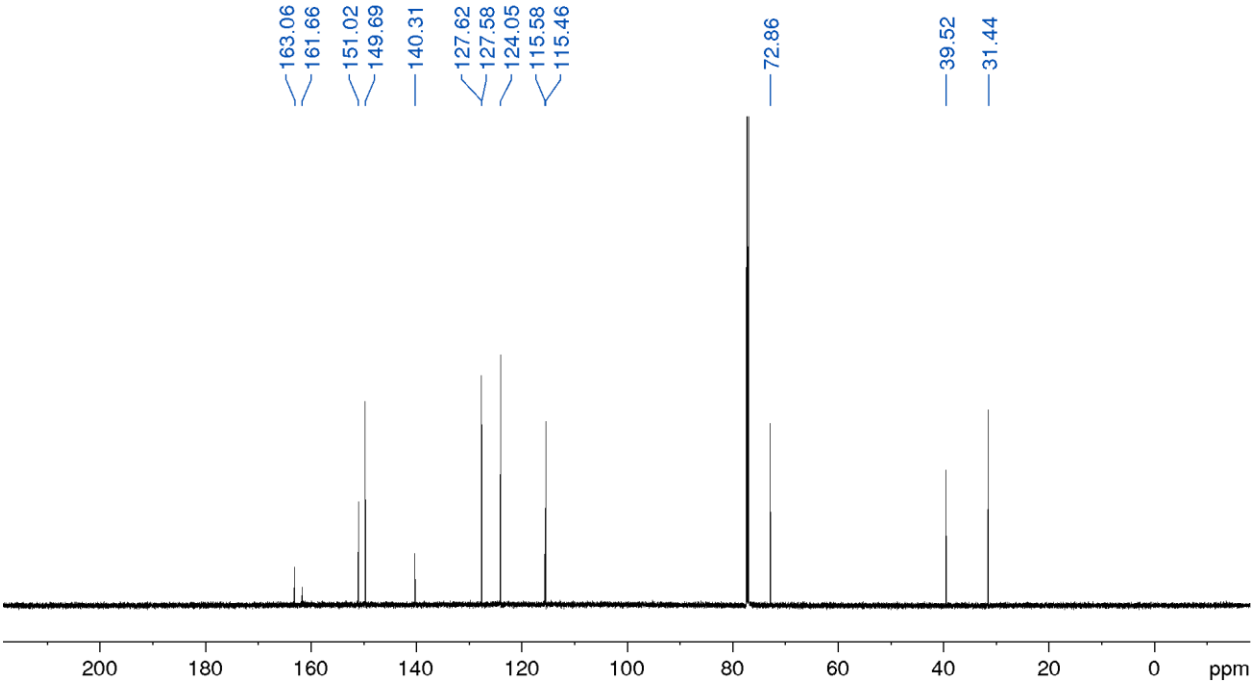
$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **1t**



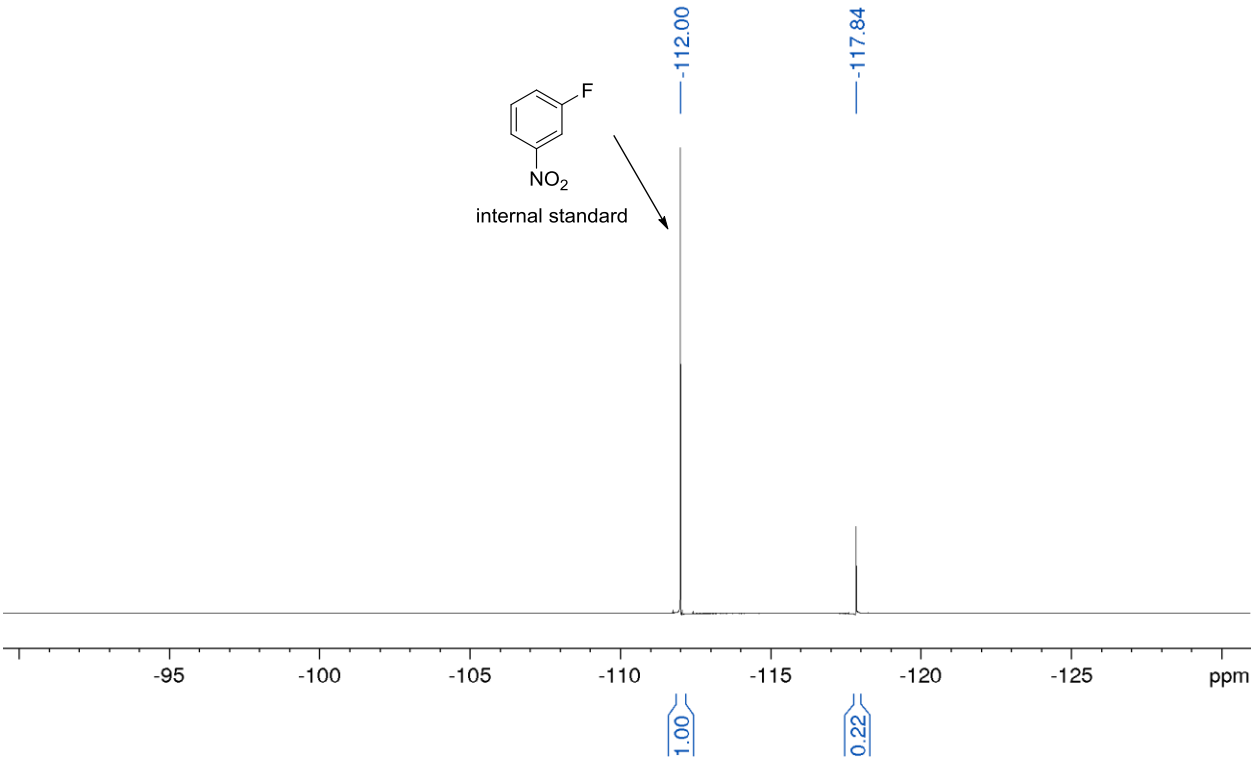

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3a**



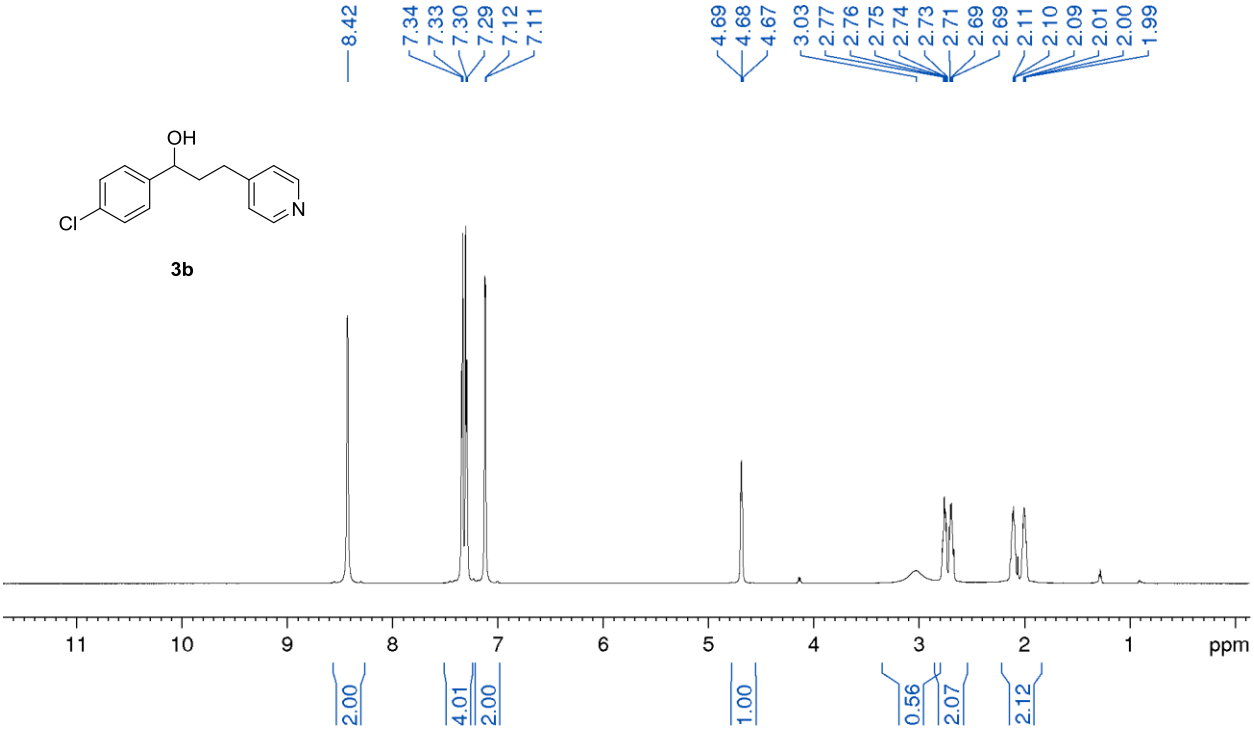
$^{13}C$ NMR (176 MHz, $CDCl_3$) of **3a**



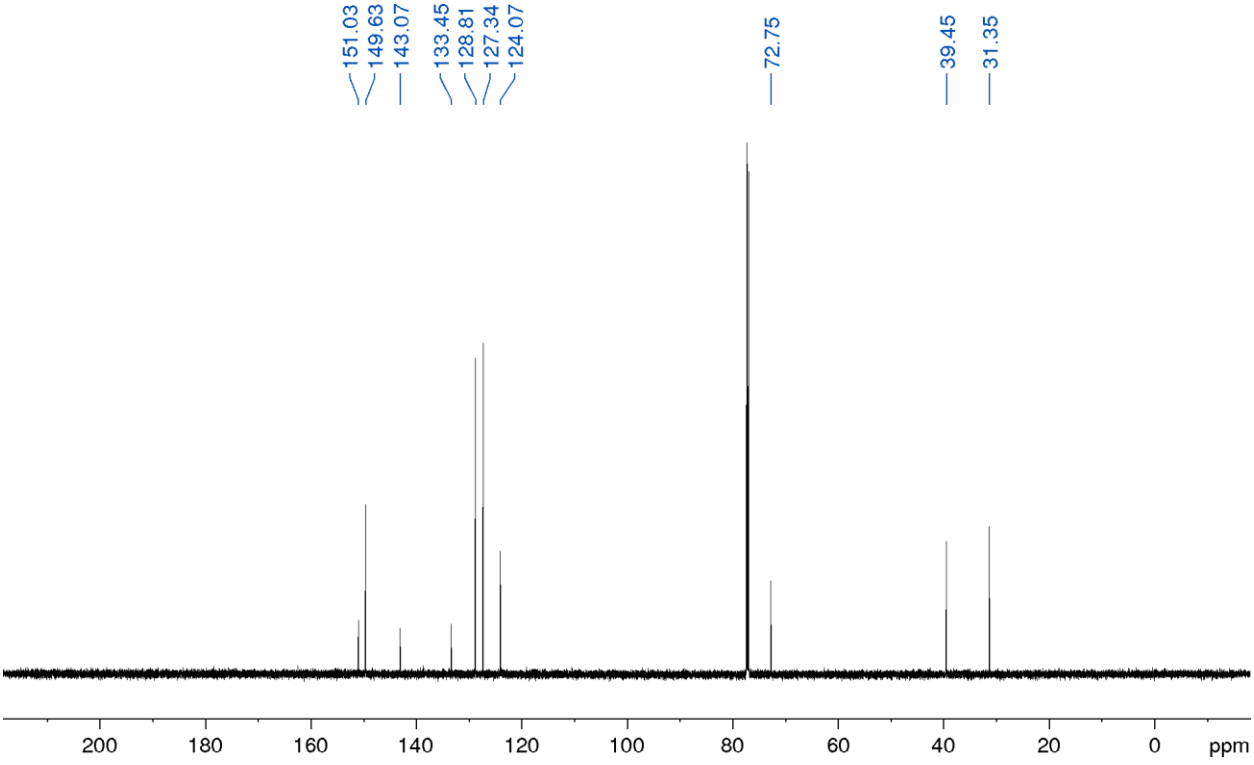

$^{19}F$ NMR (700 MHz, $CDCl_3$) of **3a**



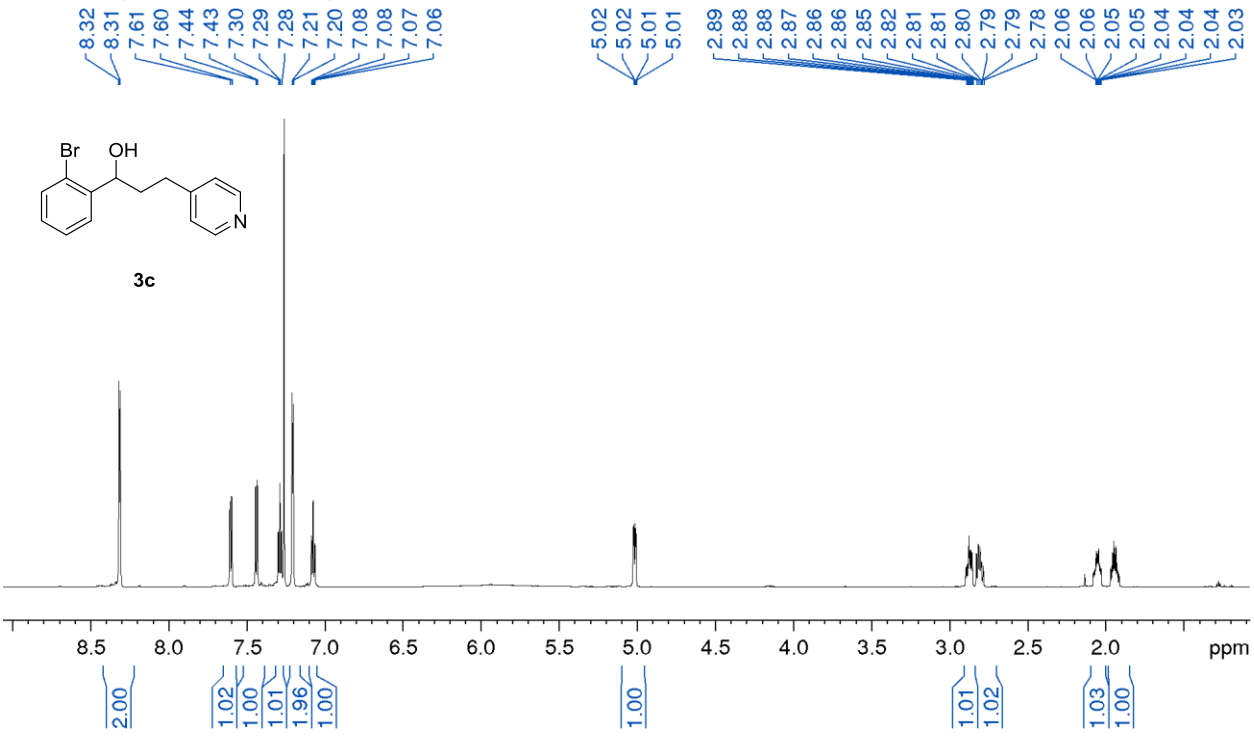
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3b**



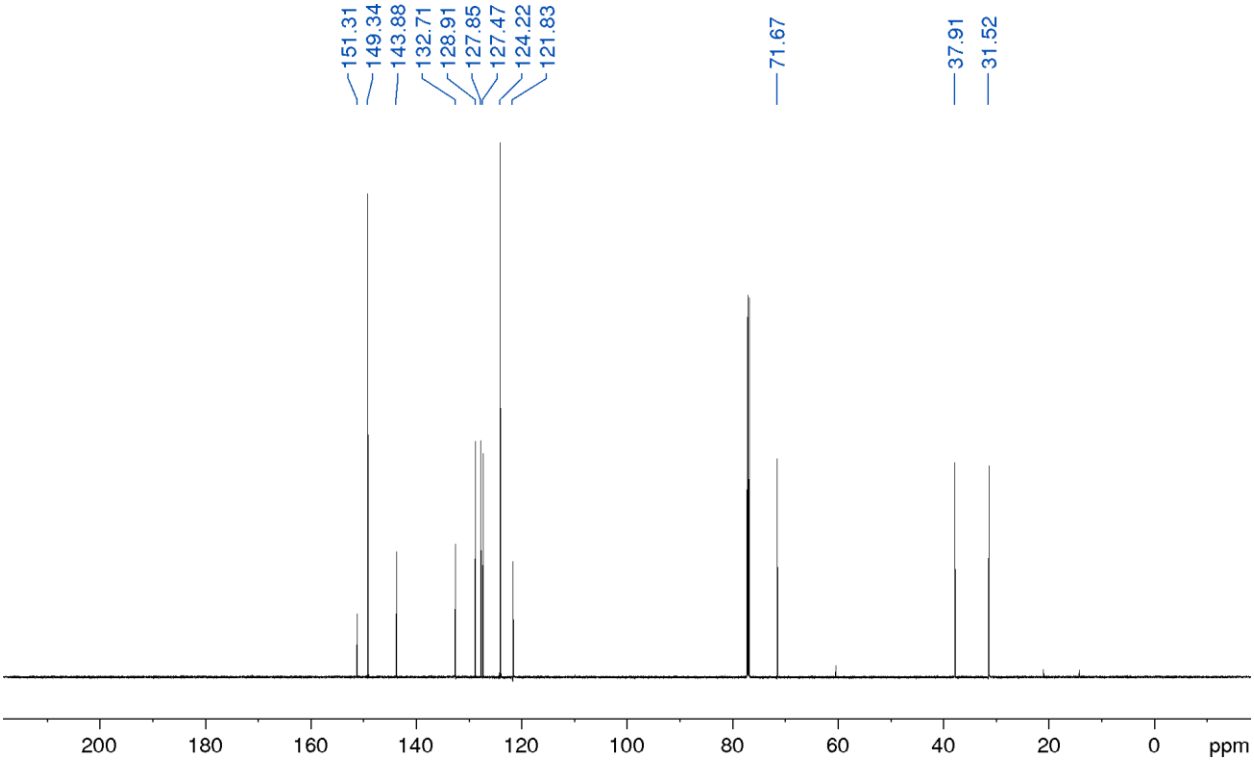

$^{13}$C NMR (176 MHz, $CDCl_3$) **of 3b**



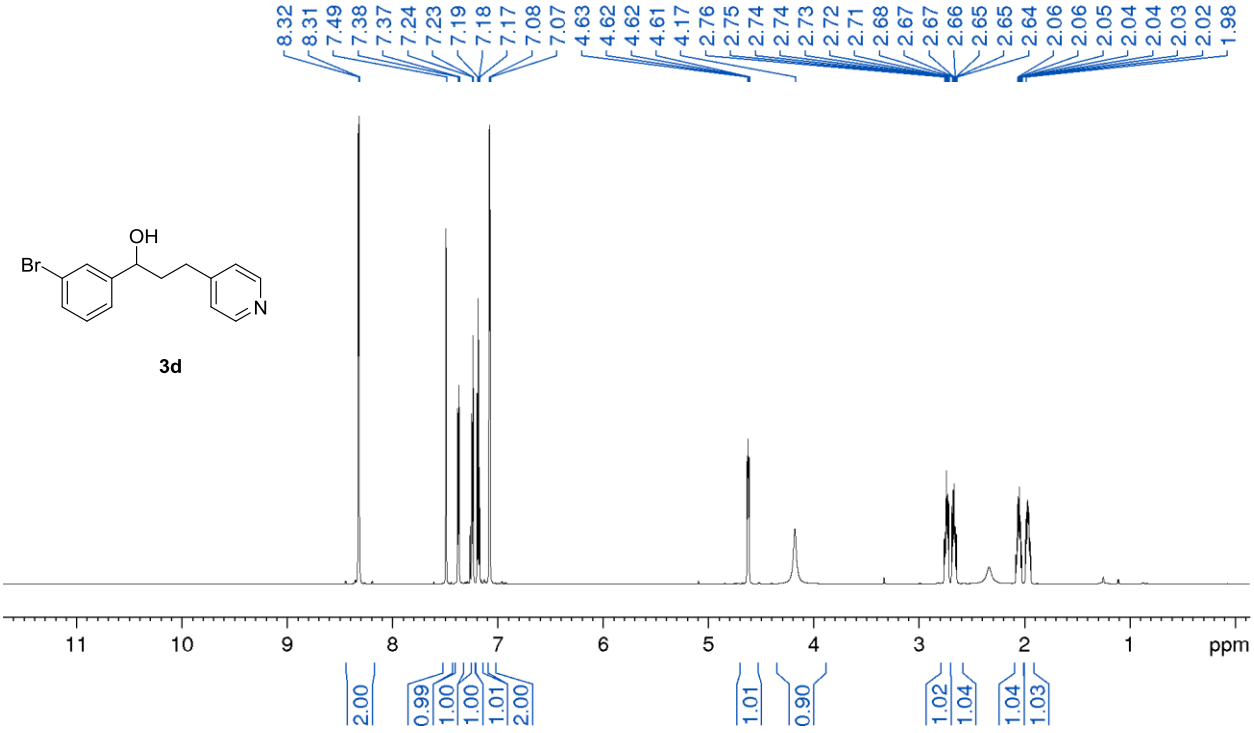
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3c**



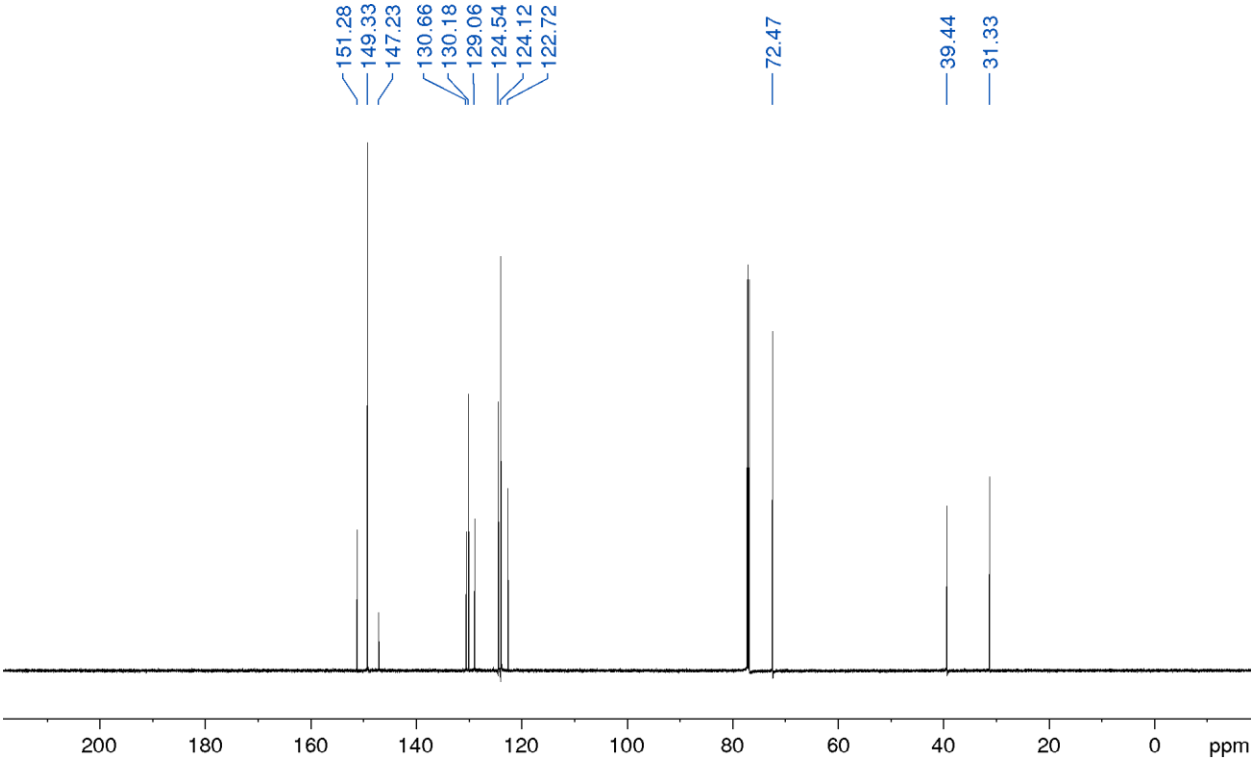

$^{13}$C NMR (176 MHz, $CDCl_3$) of **3c**



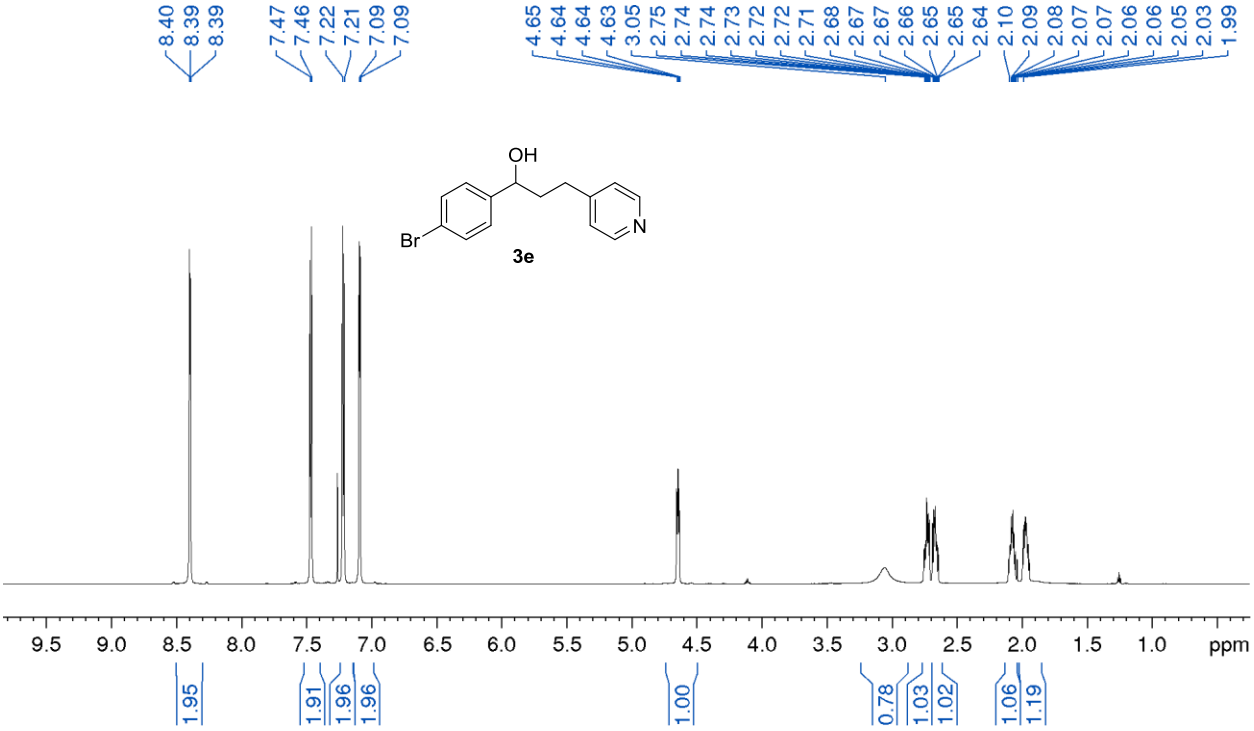
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3d**



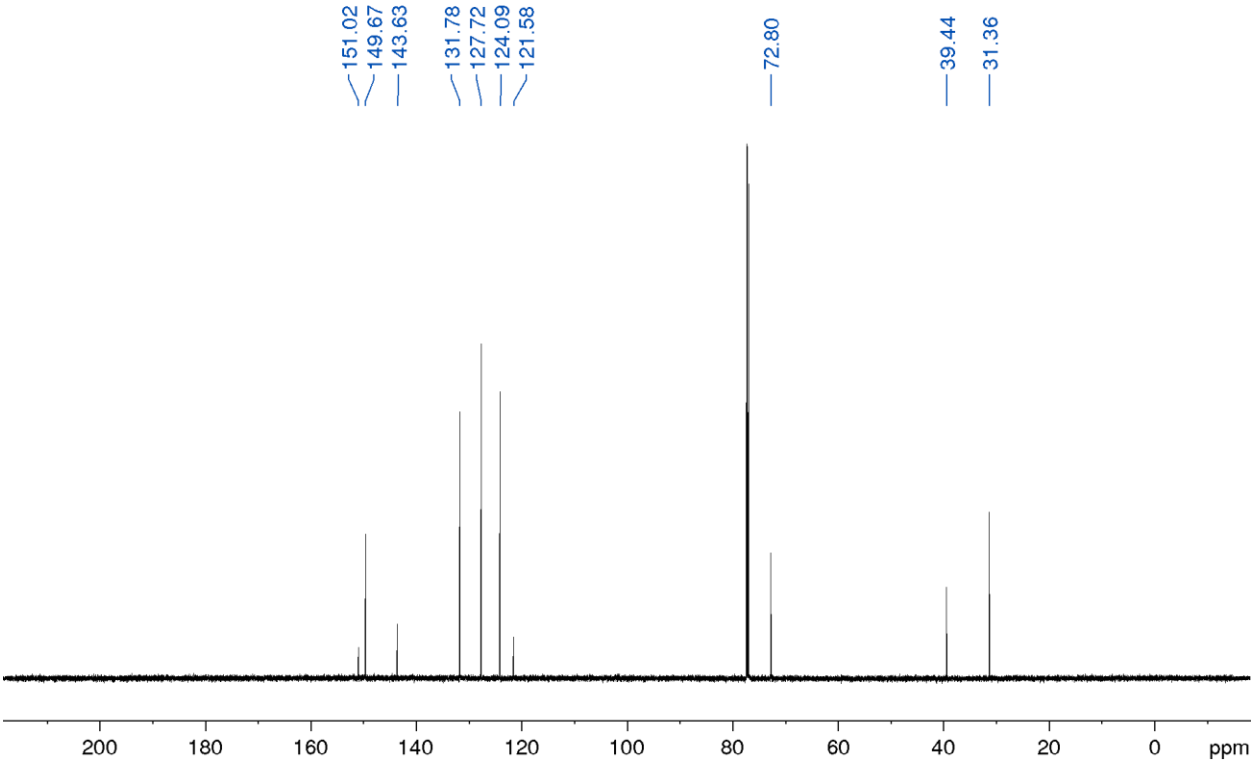

$^{13}$C NMR (176 MHz, $CDCl_3$) of **3d**



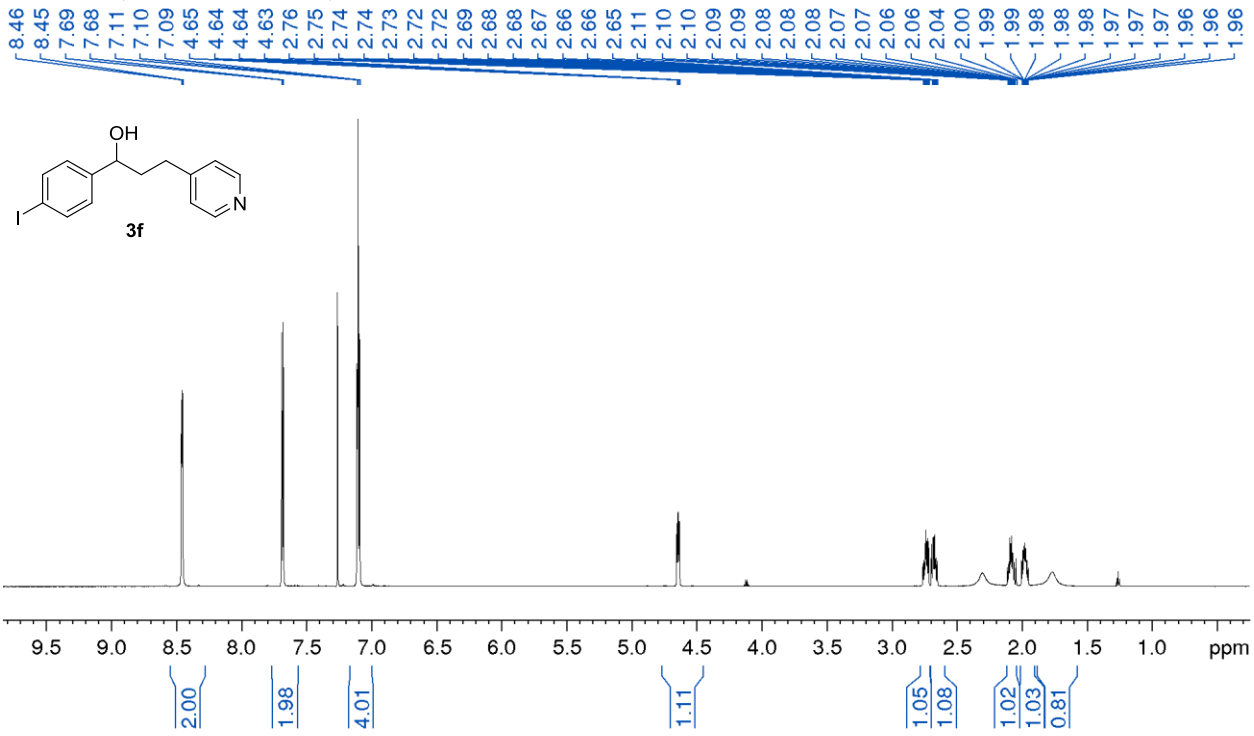
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3e**



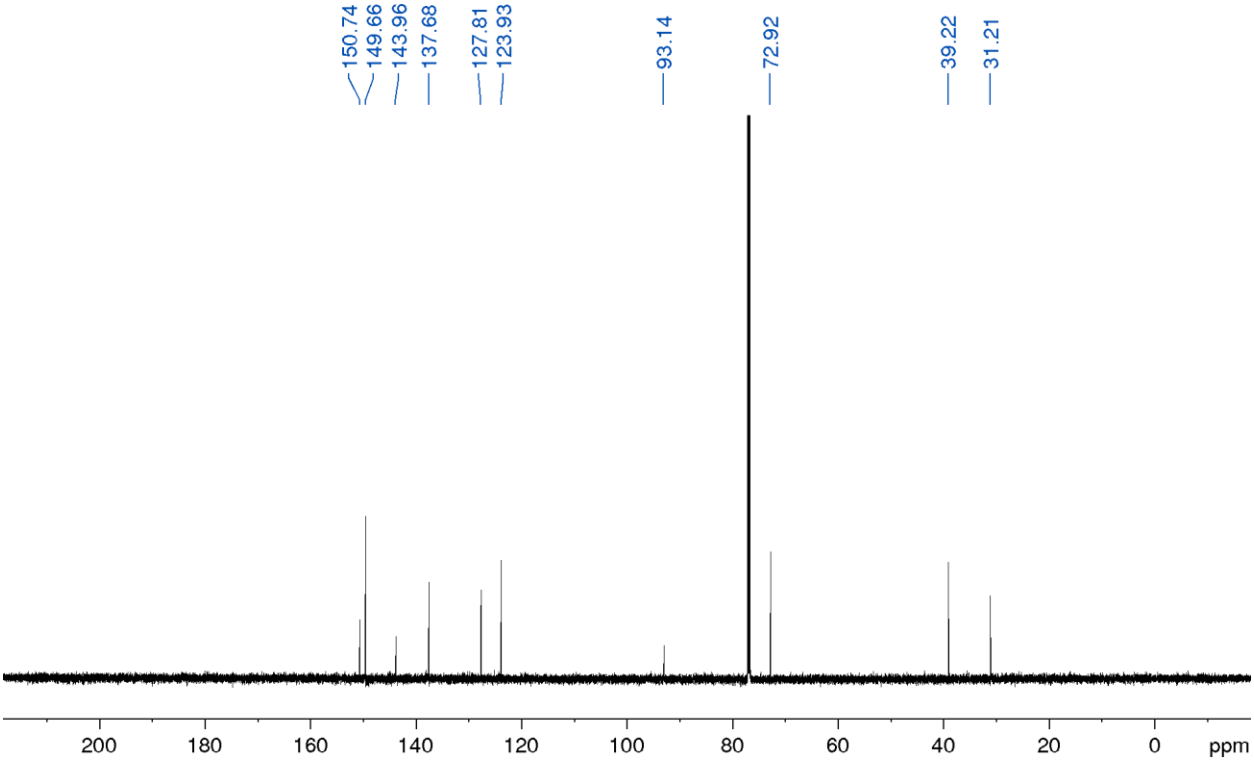

**$^{13}$C NMR (176 MHz, $CDCl_3$) of 3e**



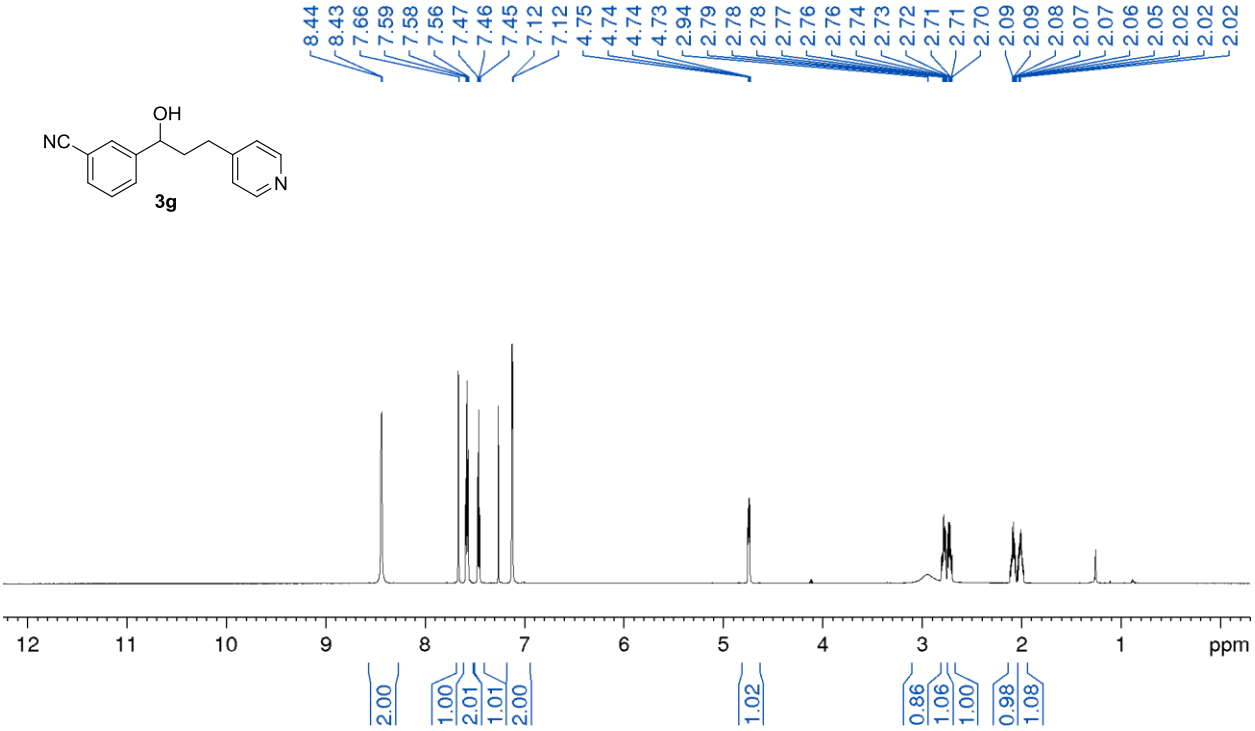
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3f**



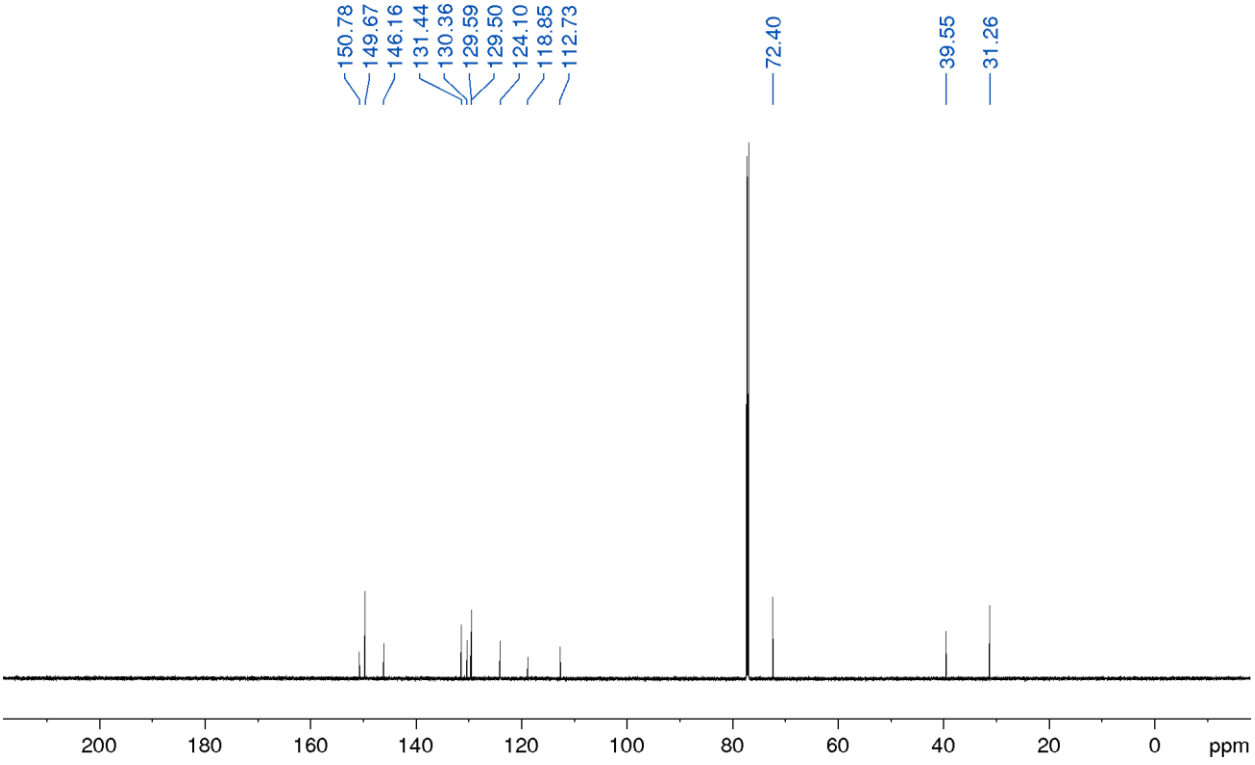

**$^{13}$C NMR (176 MHz, $CDCl_3$) of 3f**



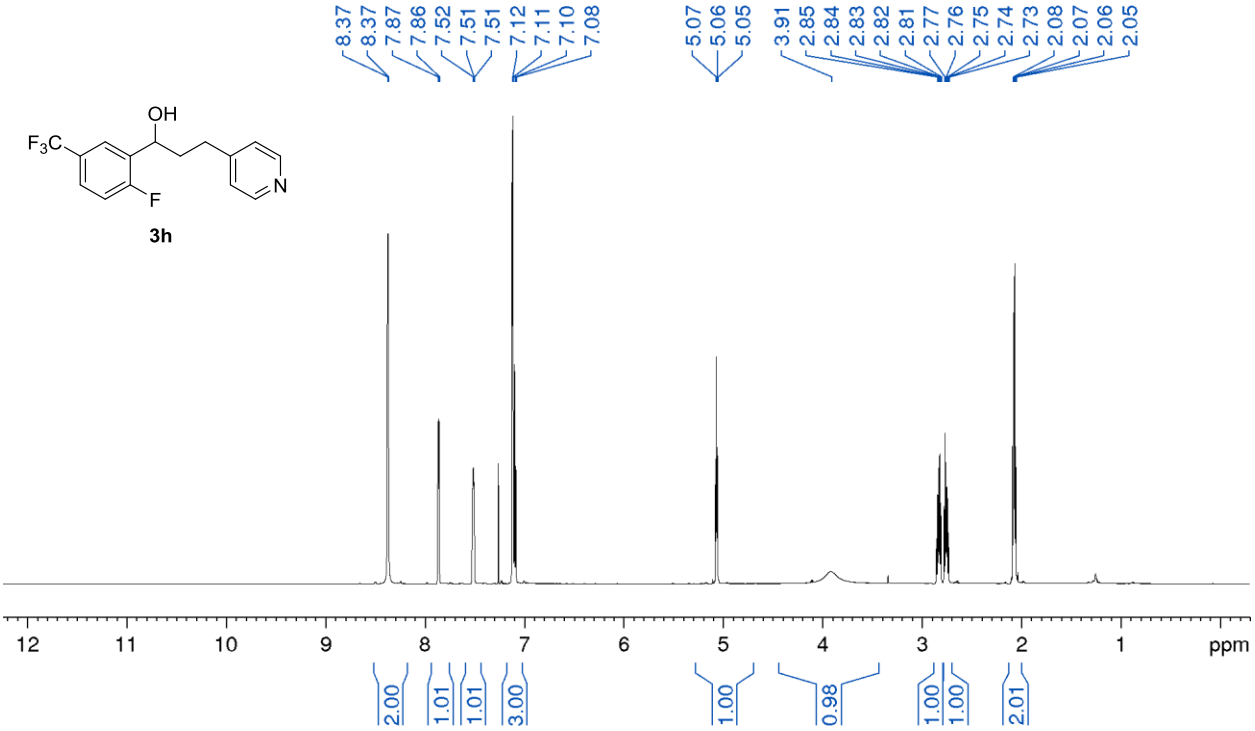
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3g**



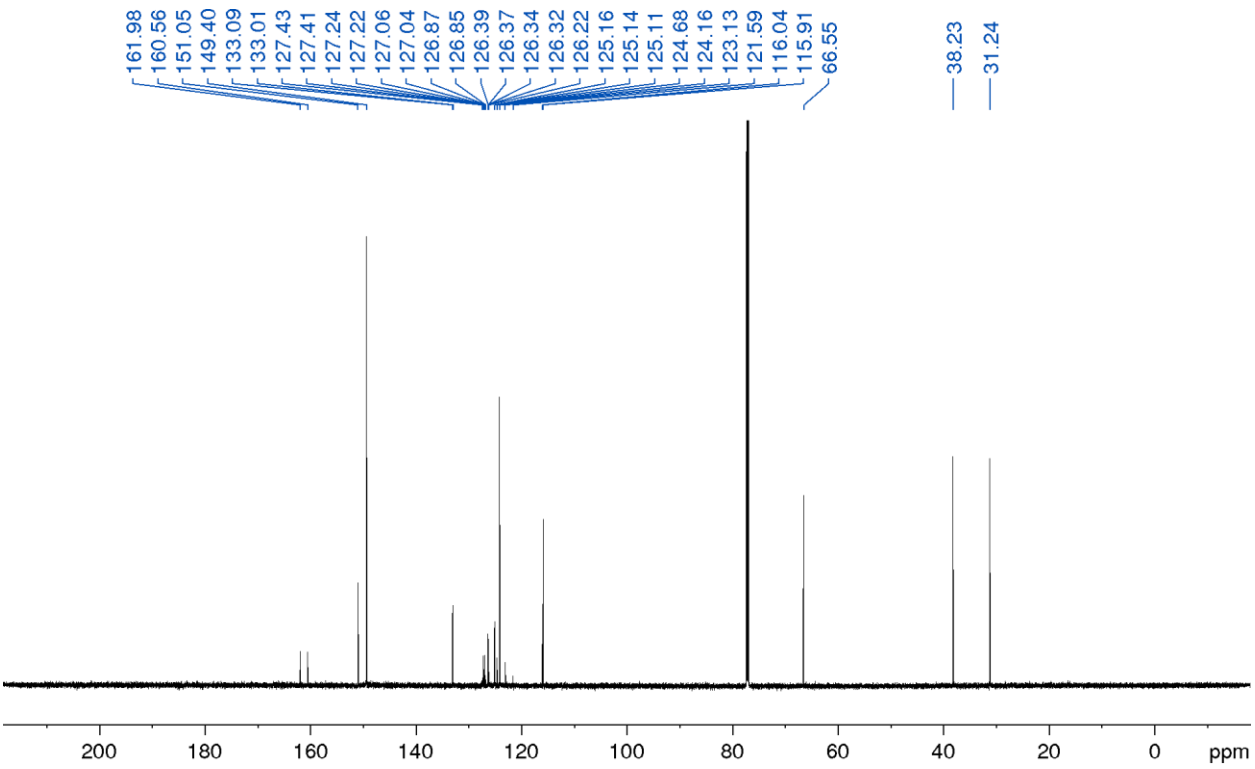

$^{13}$C NMR (176 MHz, $CDCl_3$) of **3g**



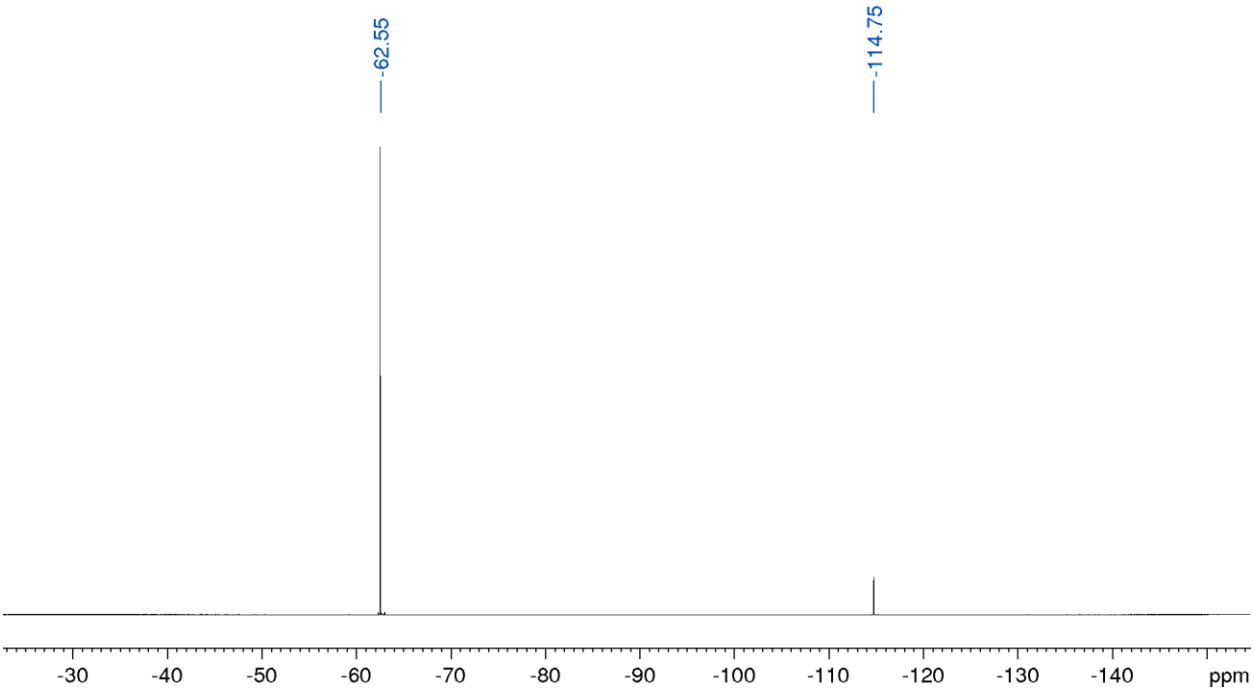
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3h**




**$^{13}$C NMR (176 MHz, $CDCl_3$) of 3h**



$^{19}F$ NMR (376 MHz, $CDCl_3$) of **3h**

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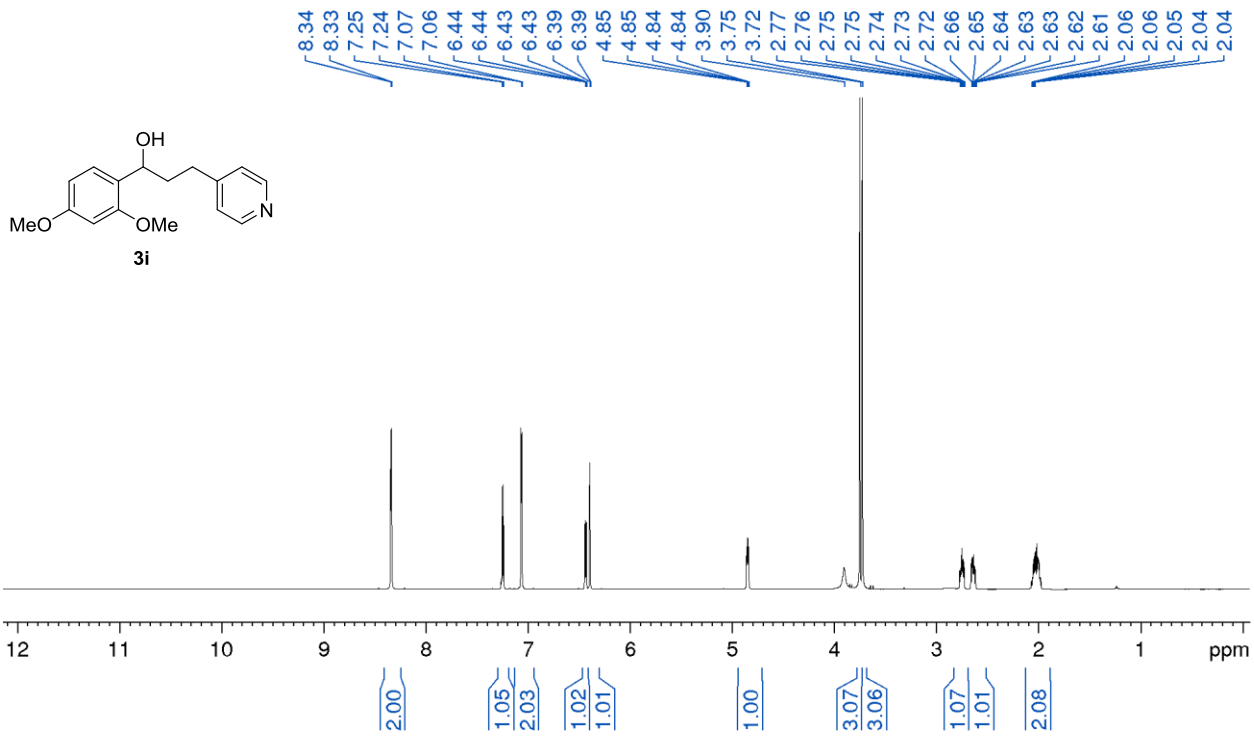
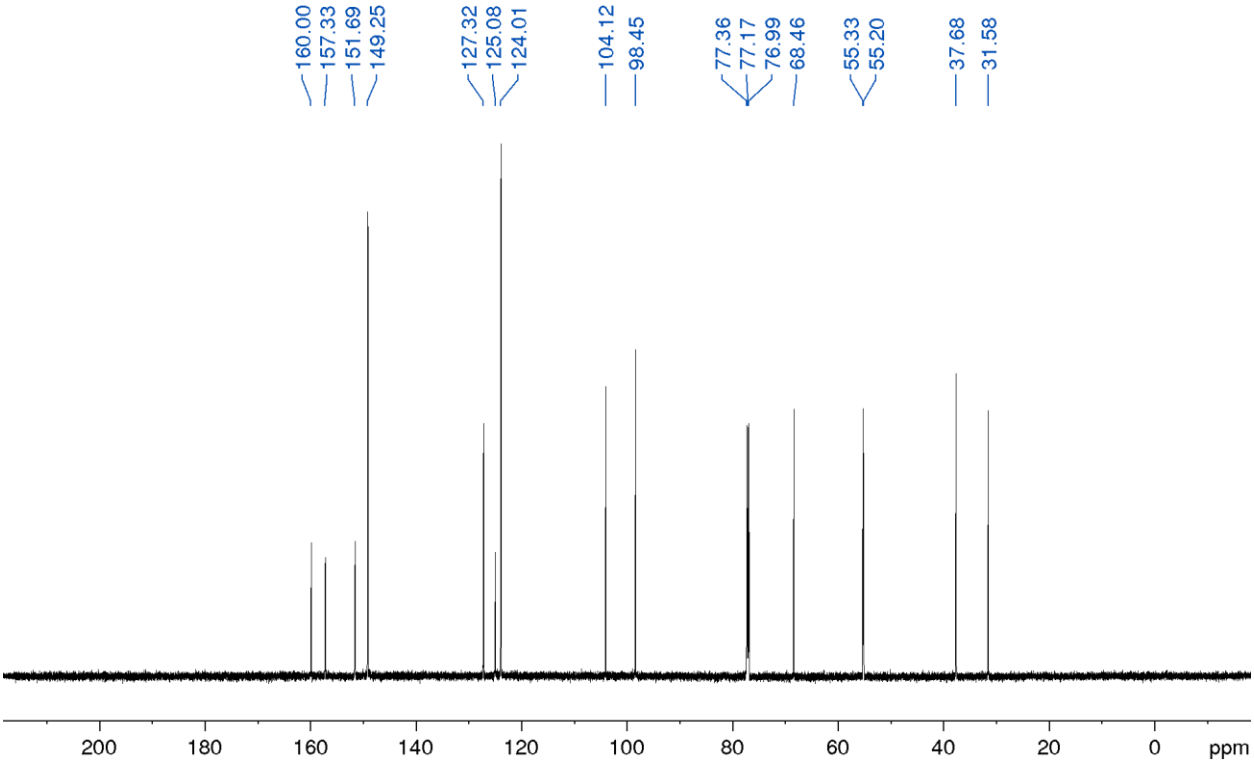
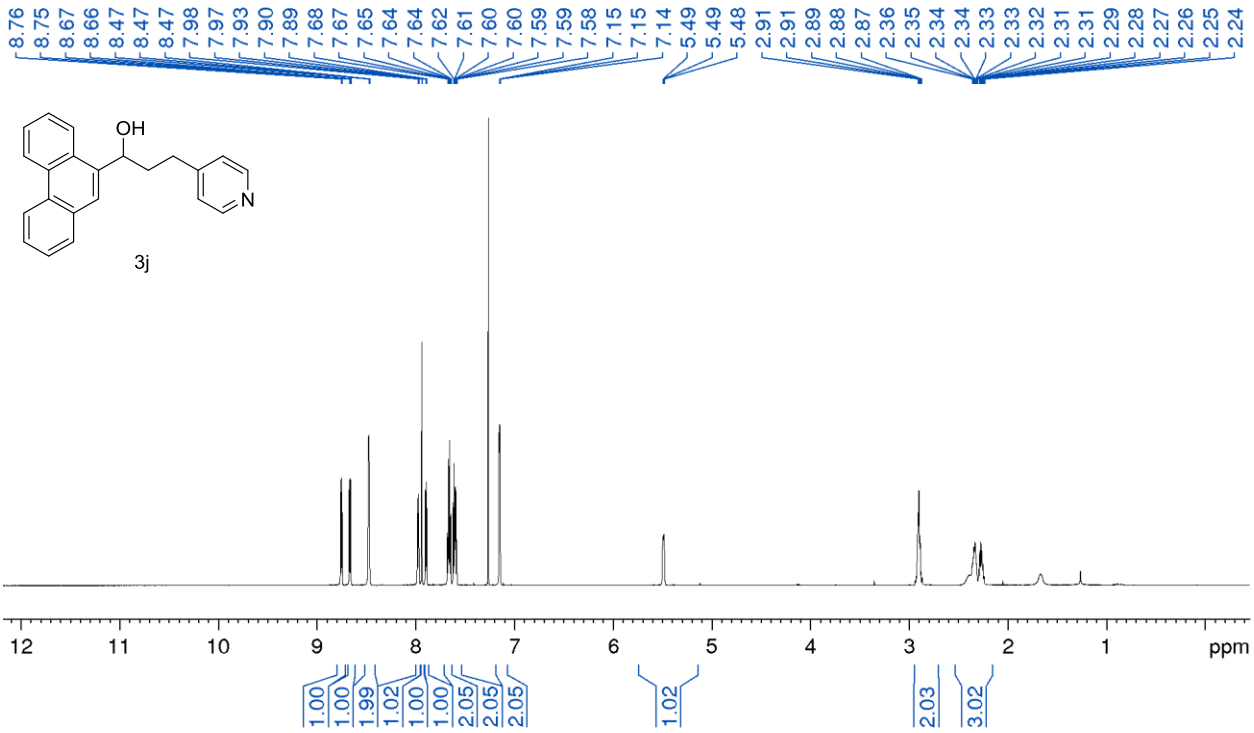


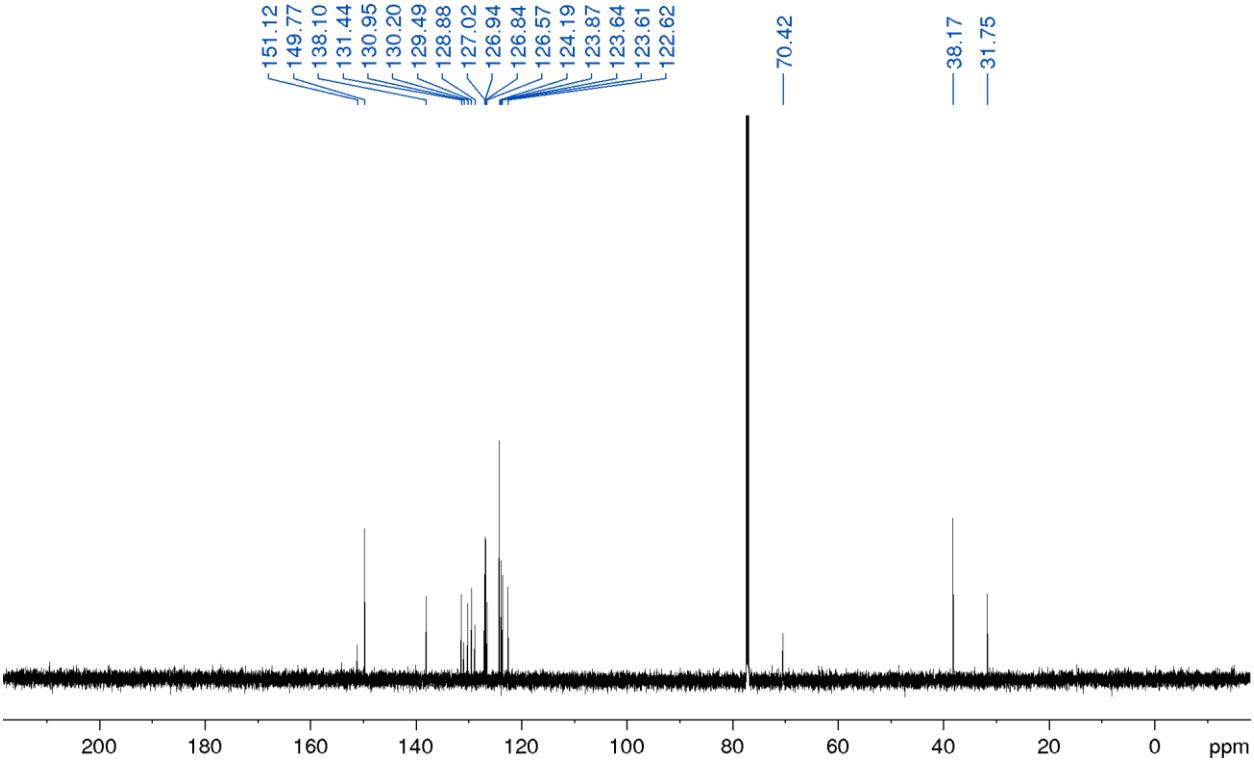
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3i**



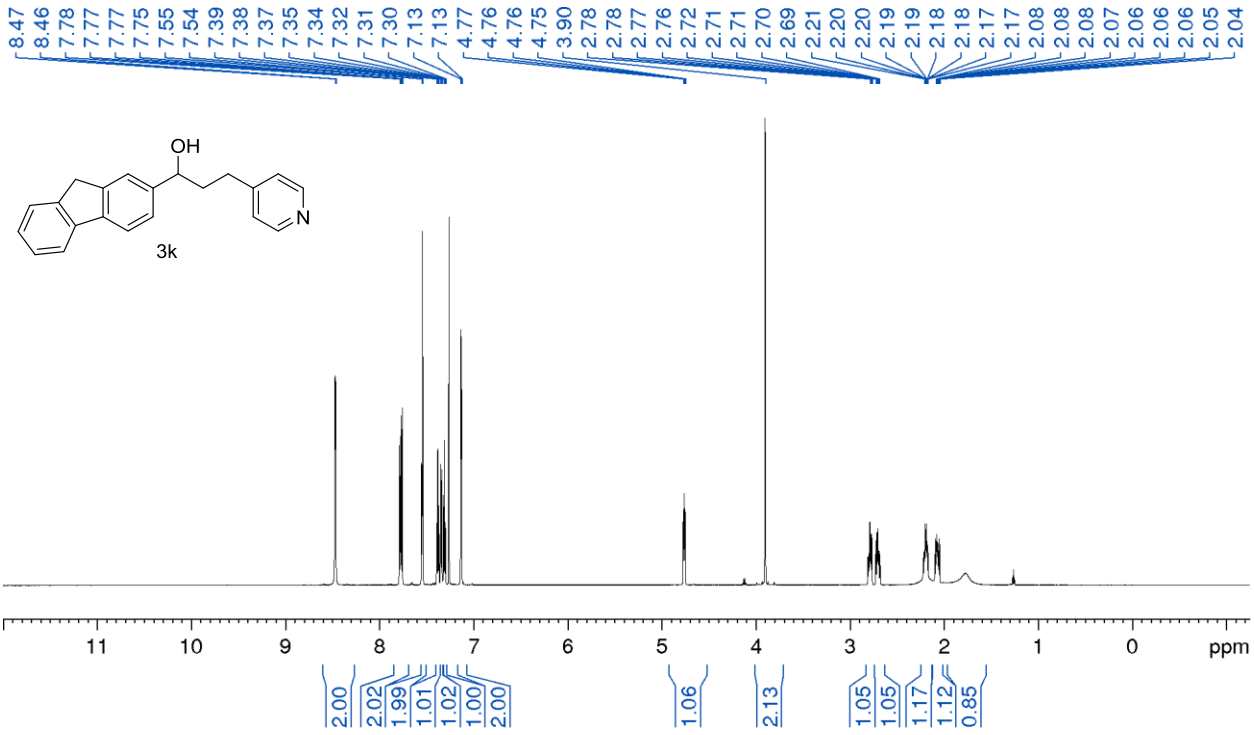

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3j**



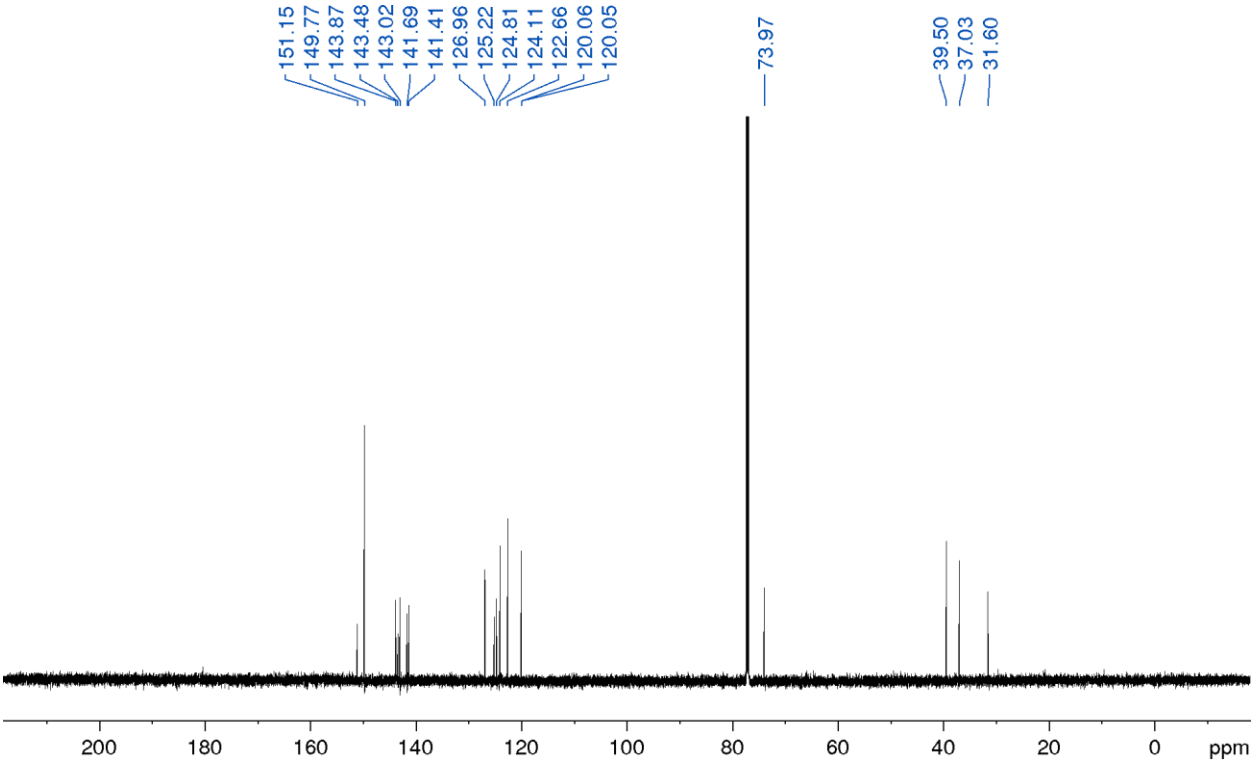
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3j**



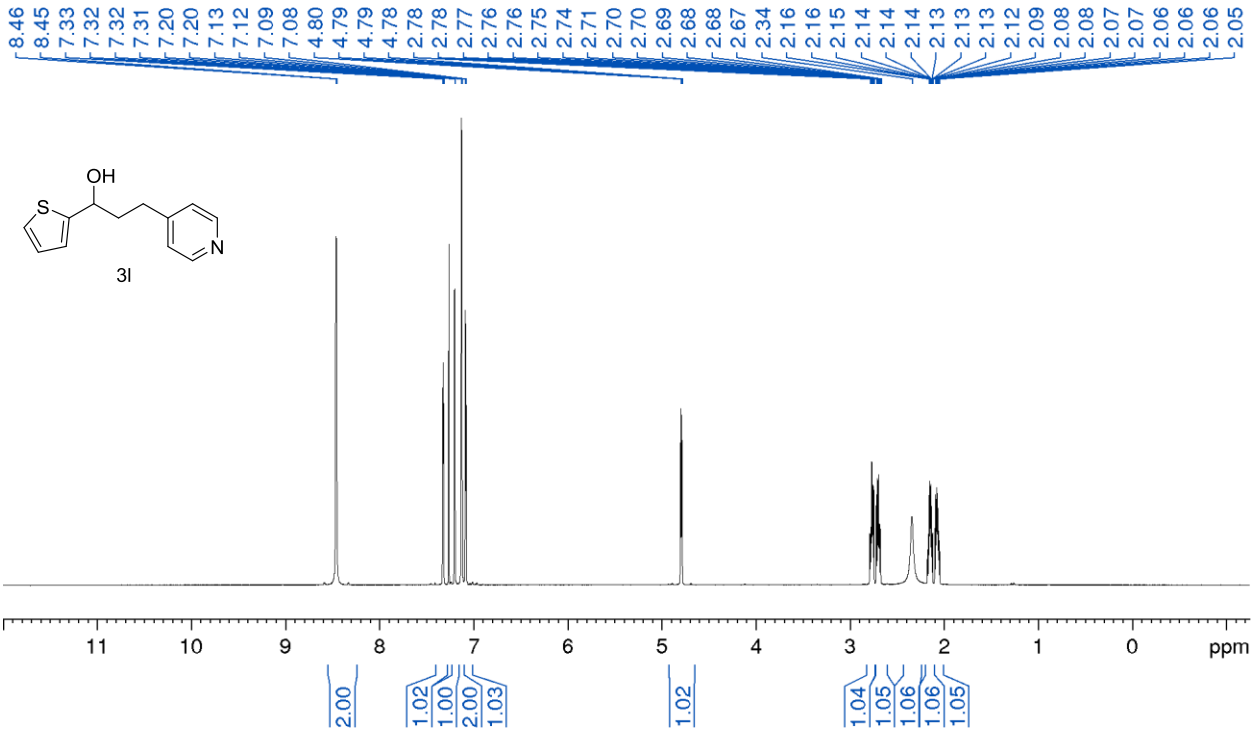

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3k**



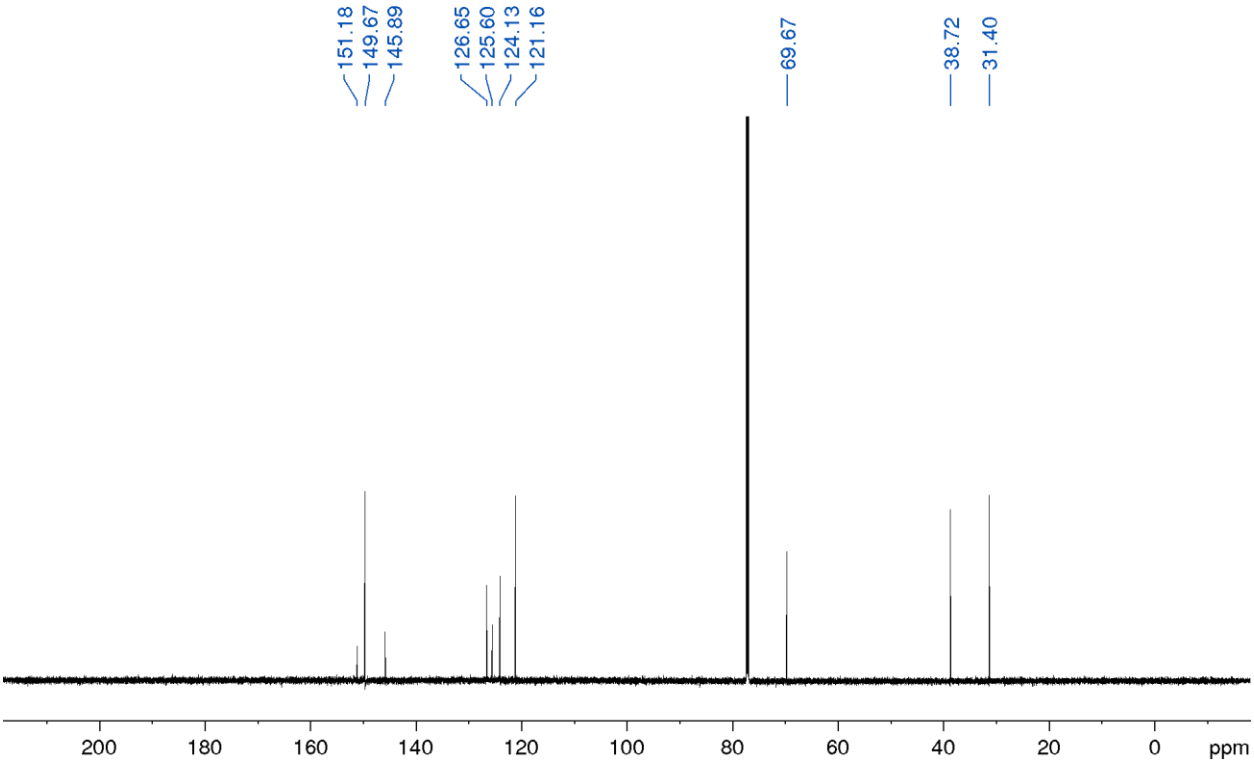
$^{13}C$ NMR (176 MHz, $CDCl_3$) of **3k**



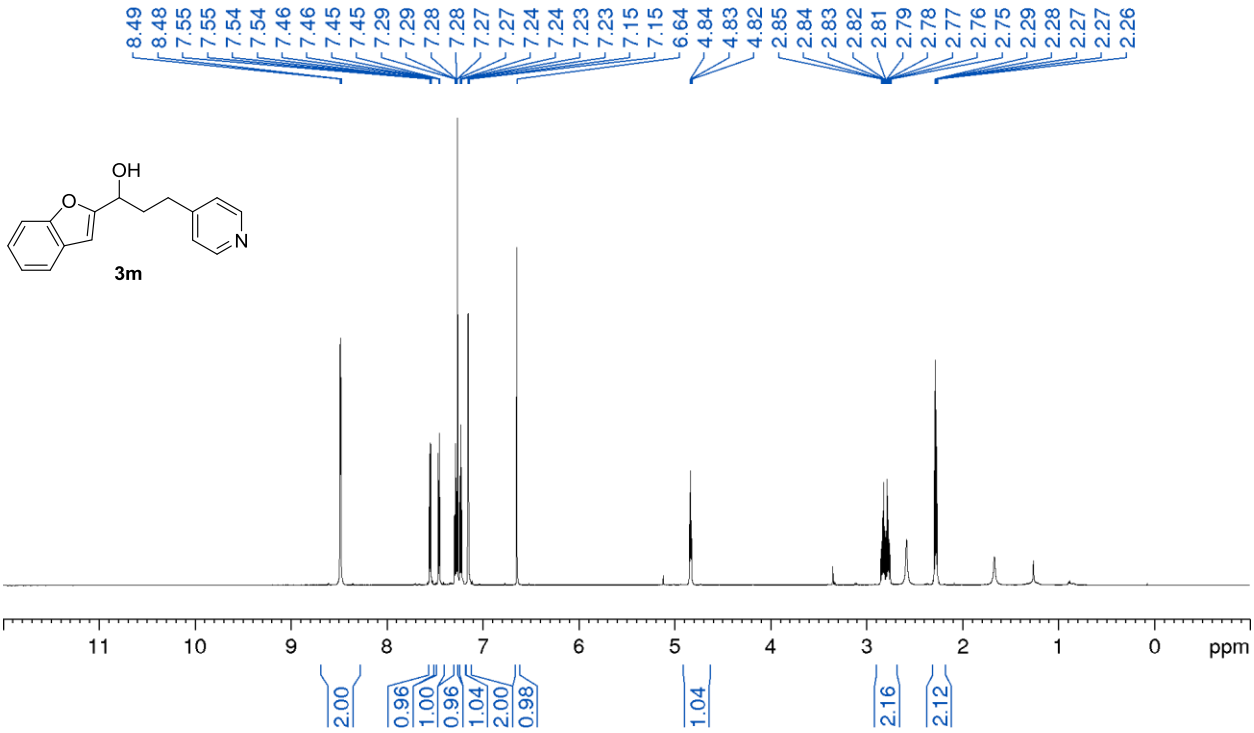

$^{1}H$ NMR (700 MHz, $CDCl_3$) **of 3l**



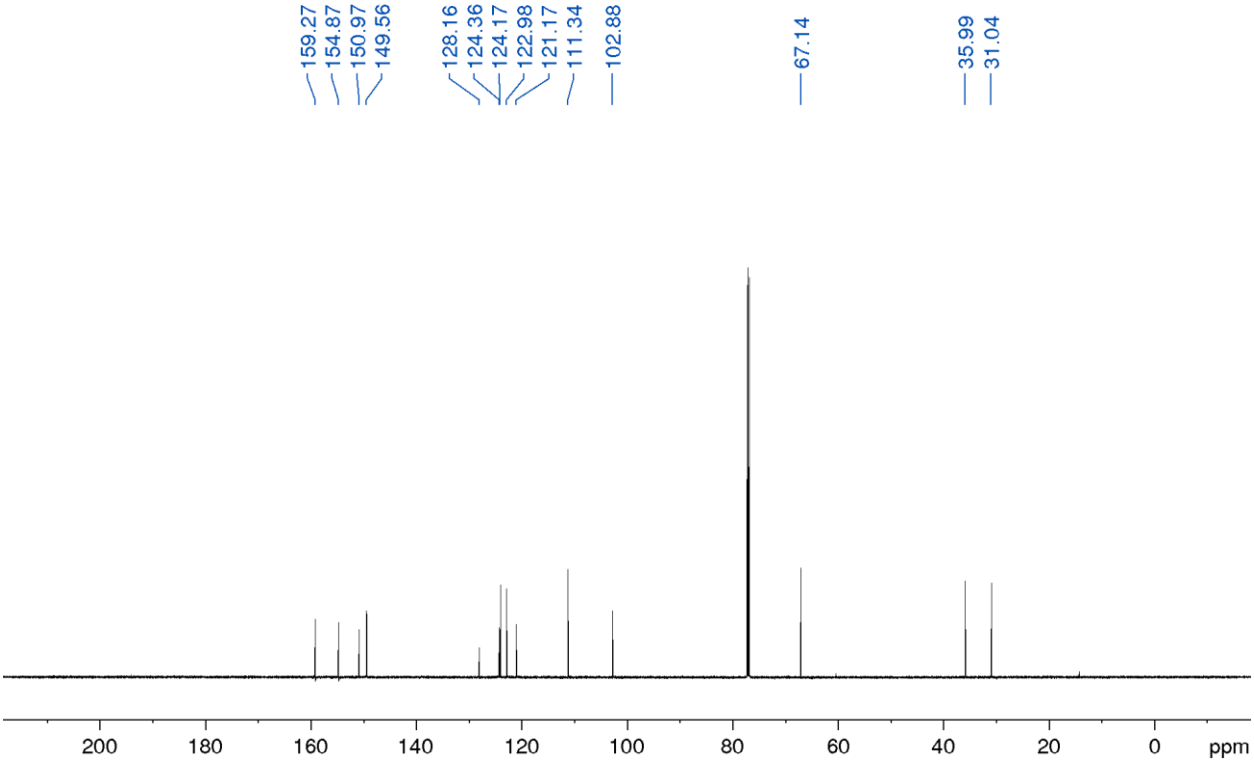
$^{13}C$ NMR (176 MHz, $CDCl_3$) of **3l**



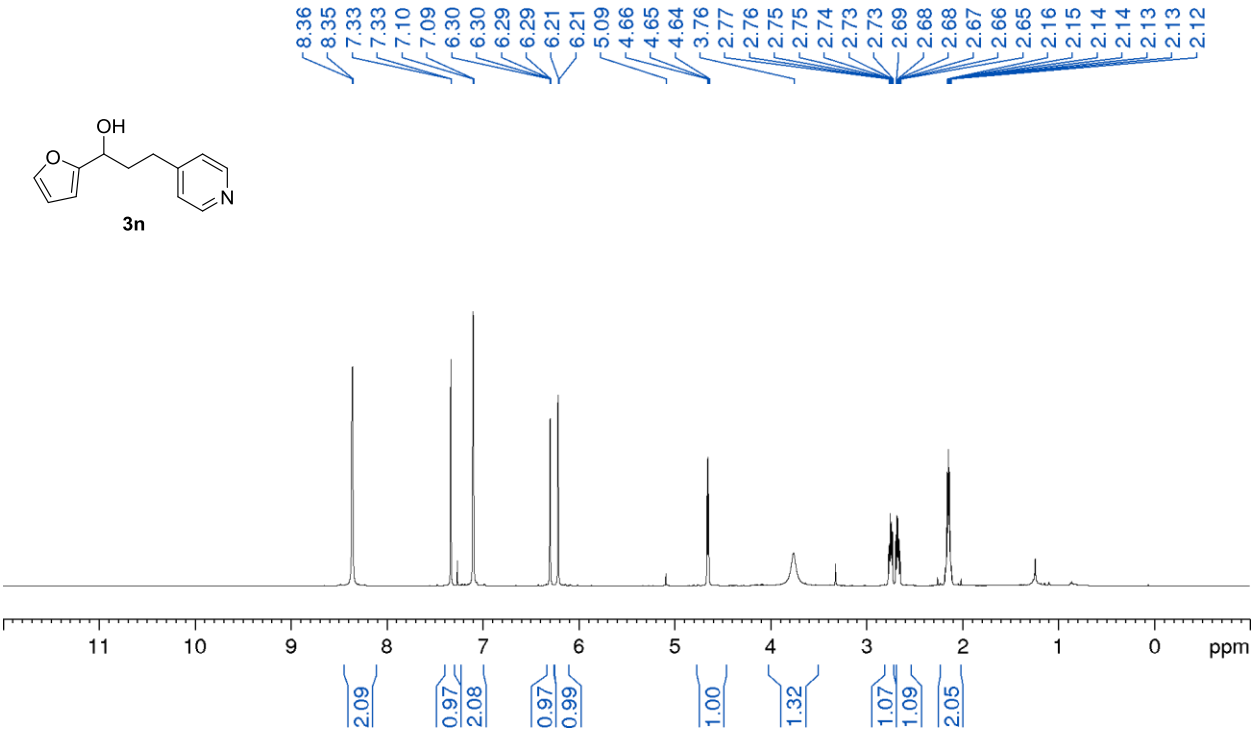

$^{1}H$ NMR (700 MHz, $CDCl_3$) of **3m**



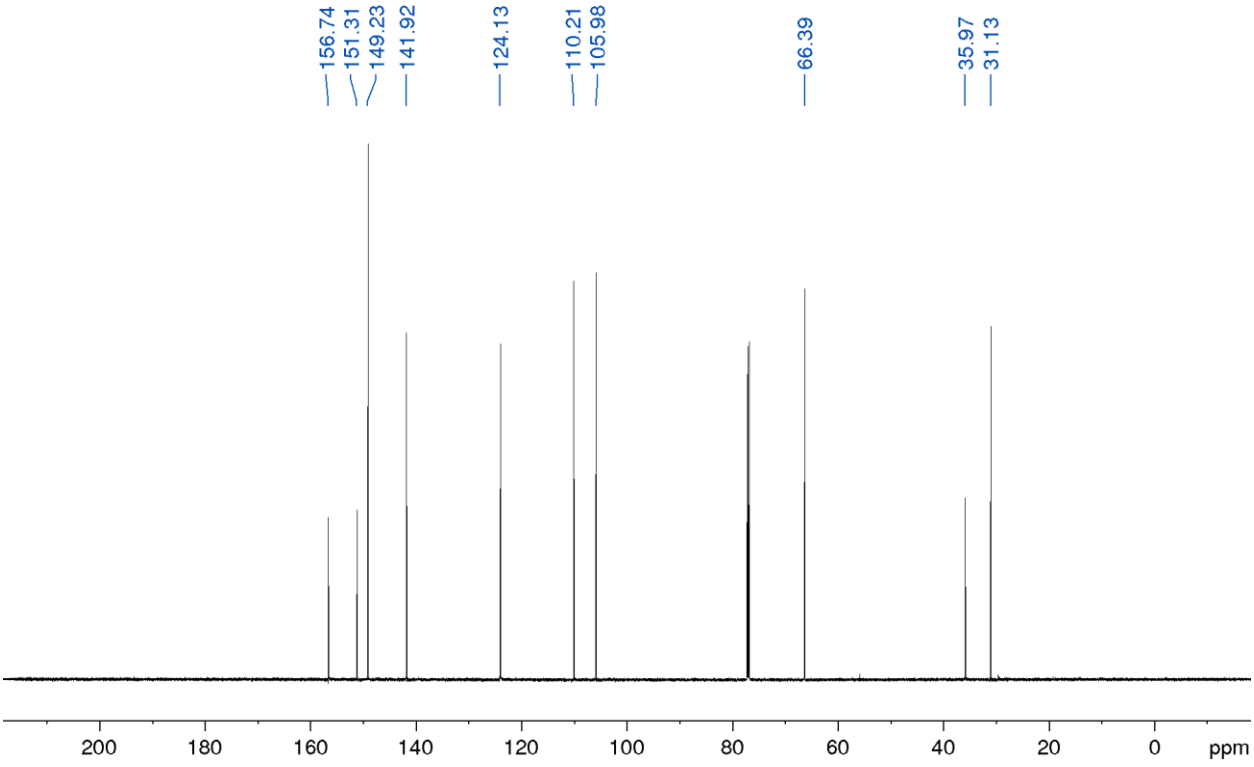
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3m**



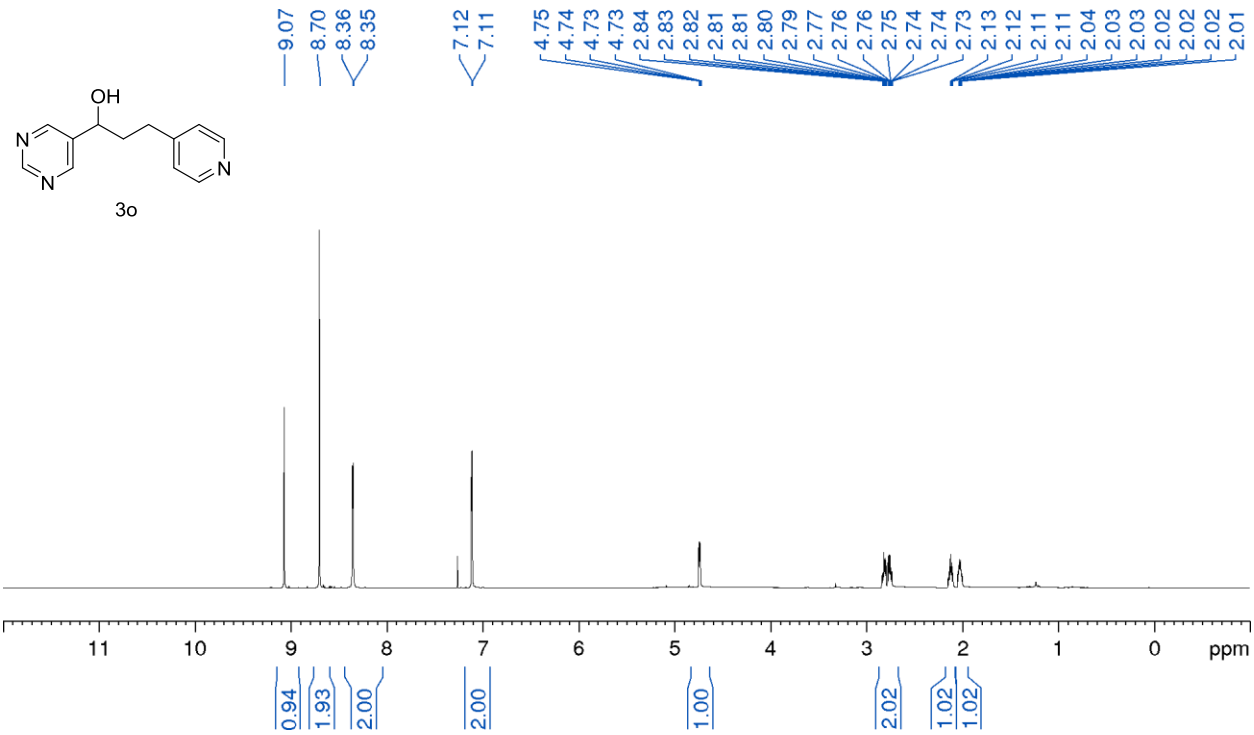

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3n**



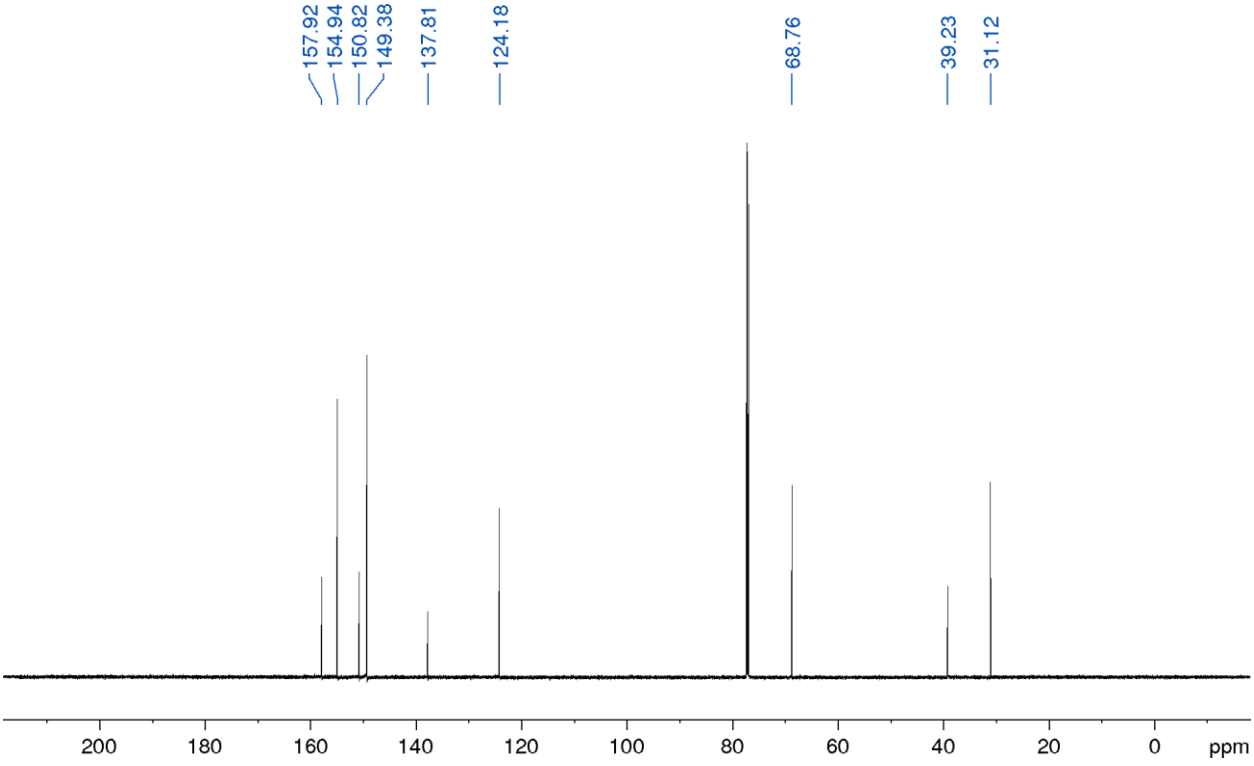
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3n**



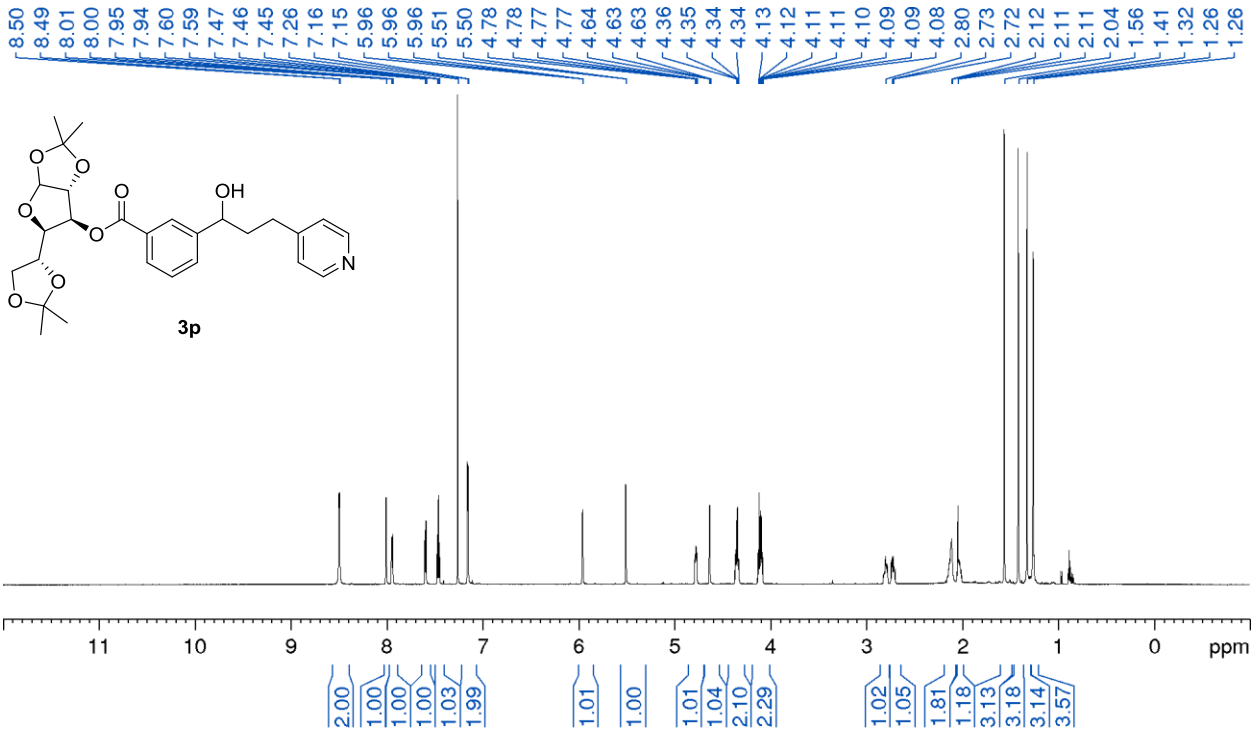

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3o**



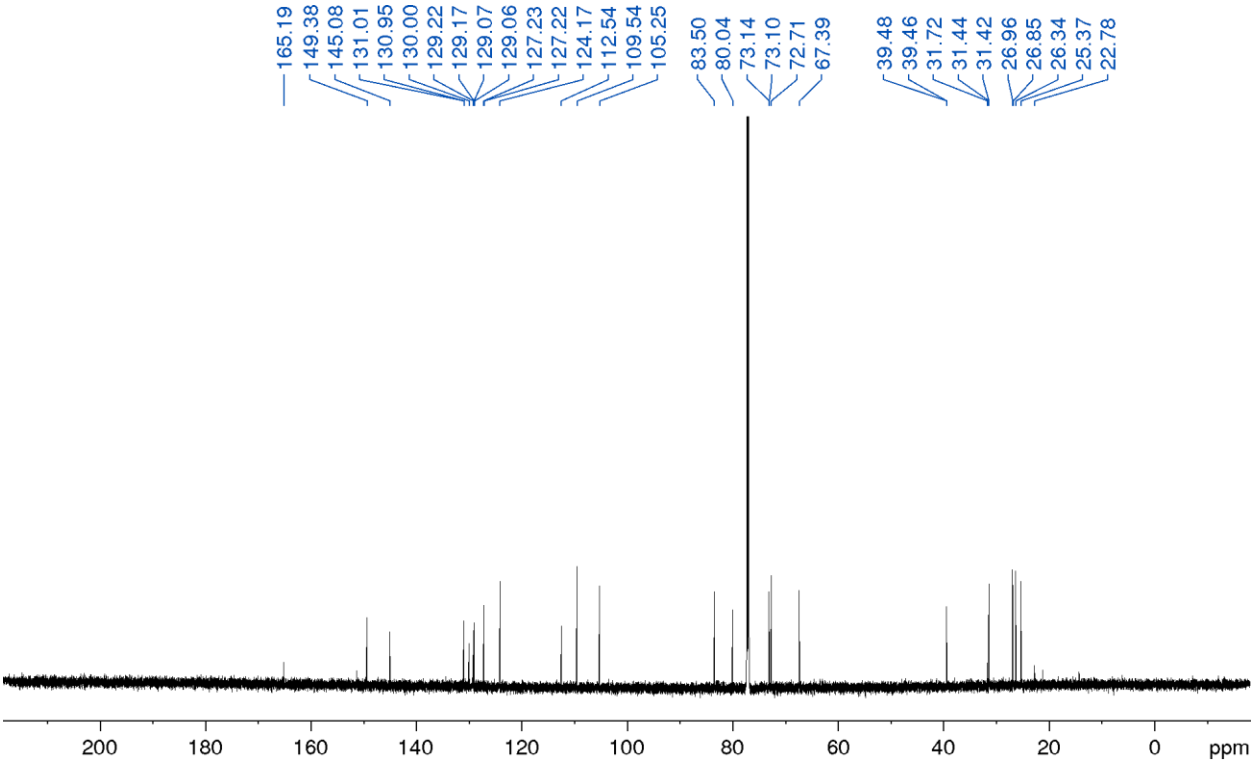
$^{13}C$ NMR (176 MHz, $CDCl_3$) of **3o**



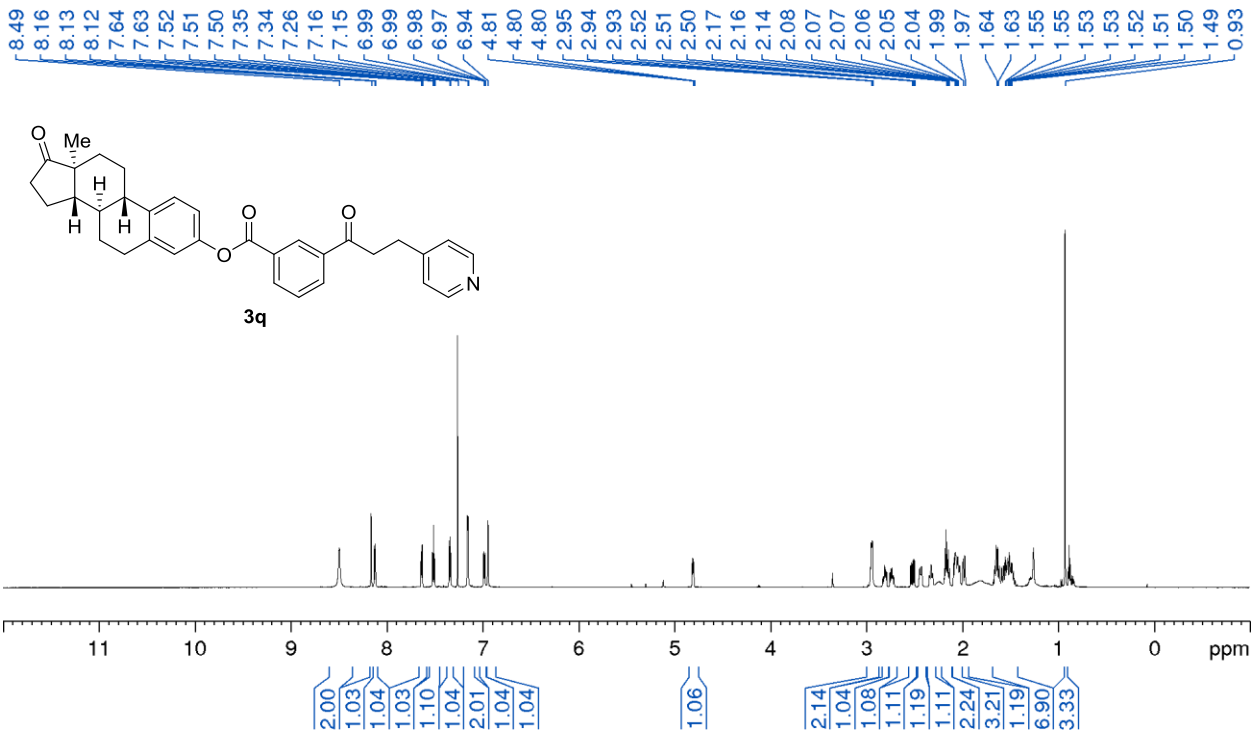

$^{1}H$ NMR (700 MHz, $CDCl_3$) of **3p**



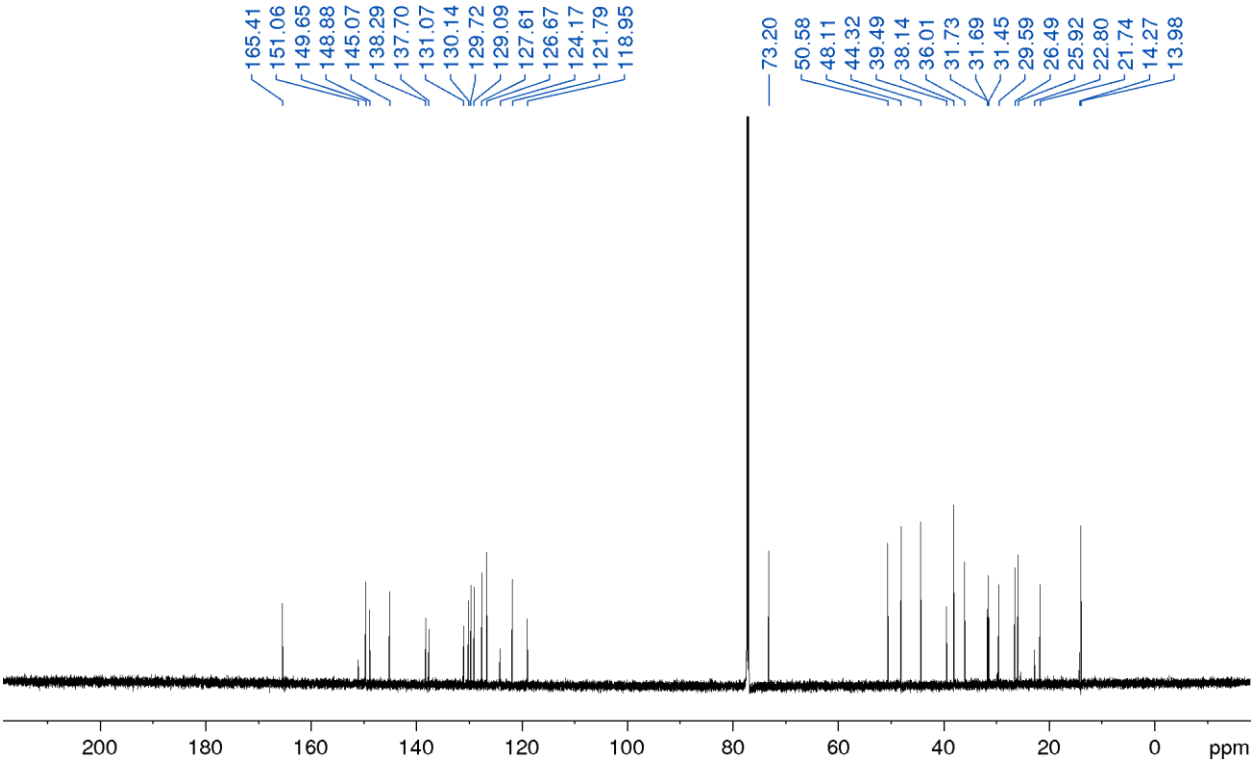
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3p**



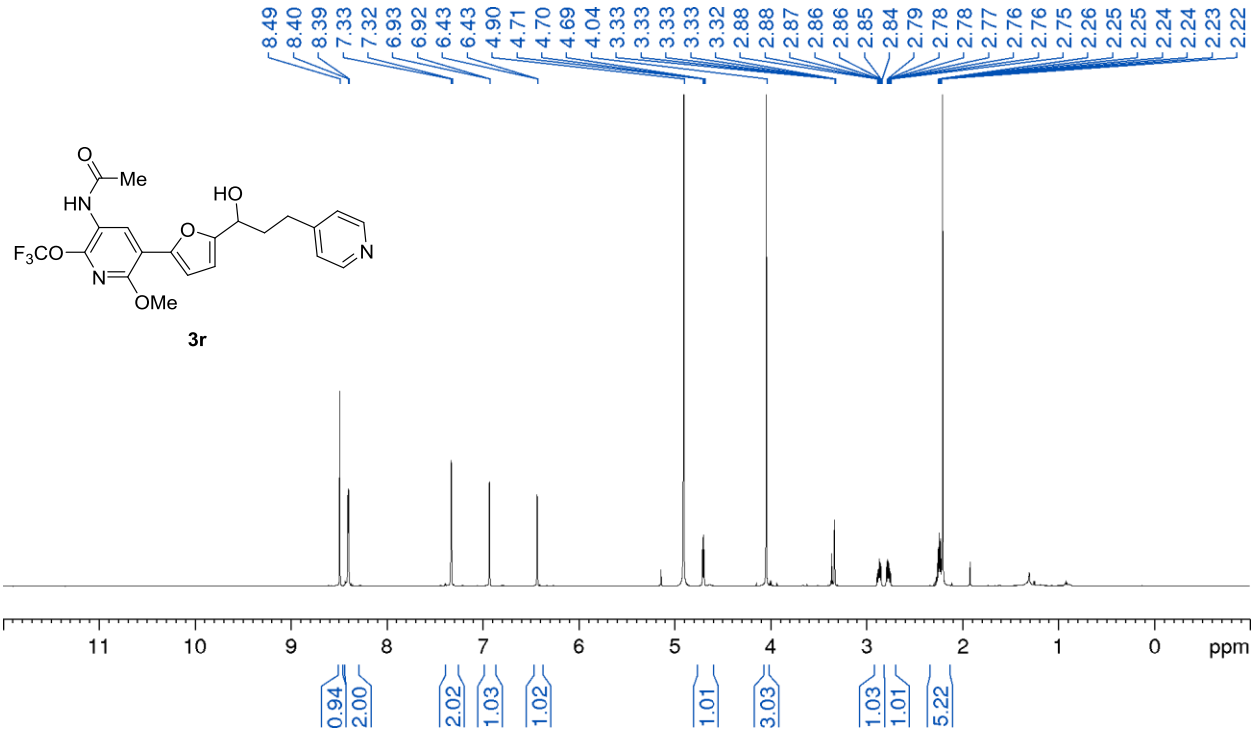

$^{1}$H NMR (700 MHz, $CDCl_3$) of **3q**



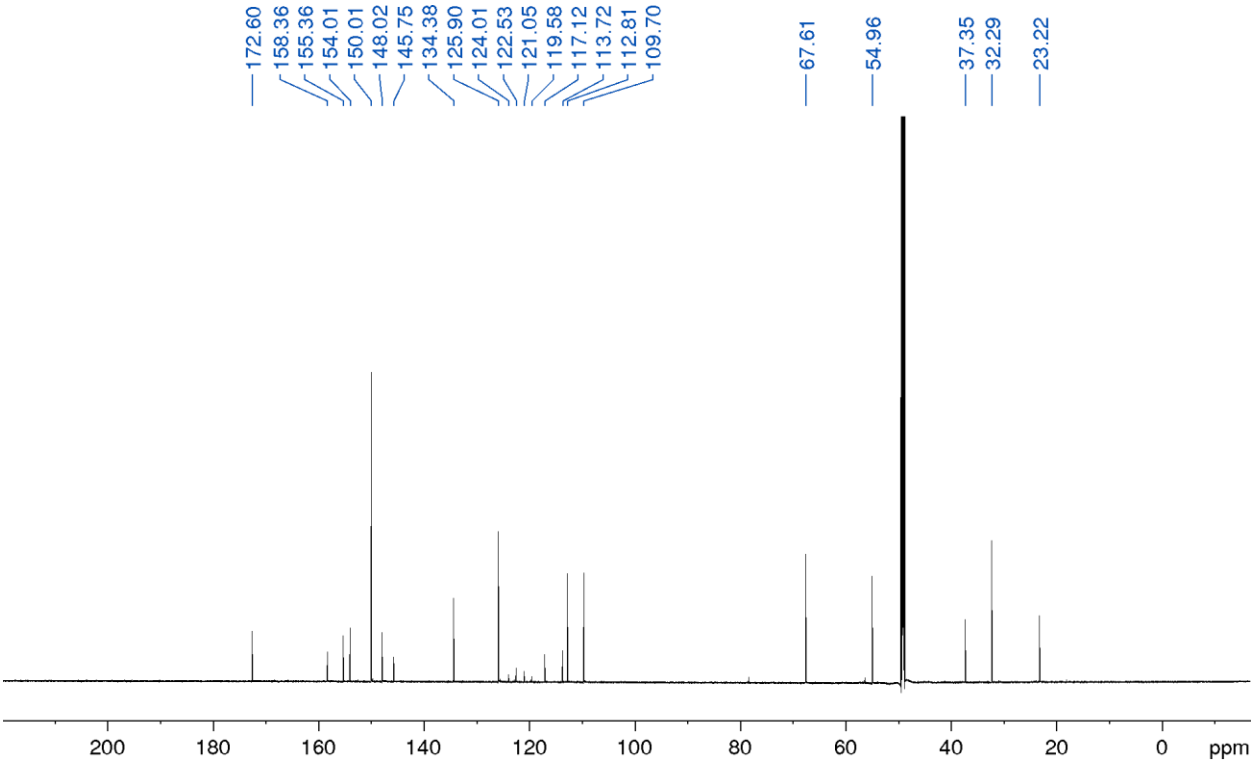
$^{13}$C NMR (176 MHz, $CDCl_3$) of **3q**



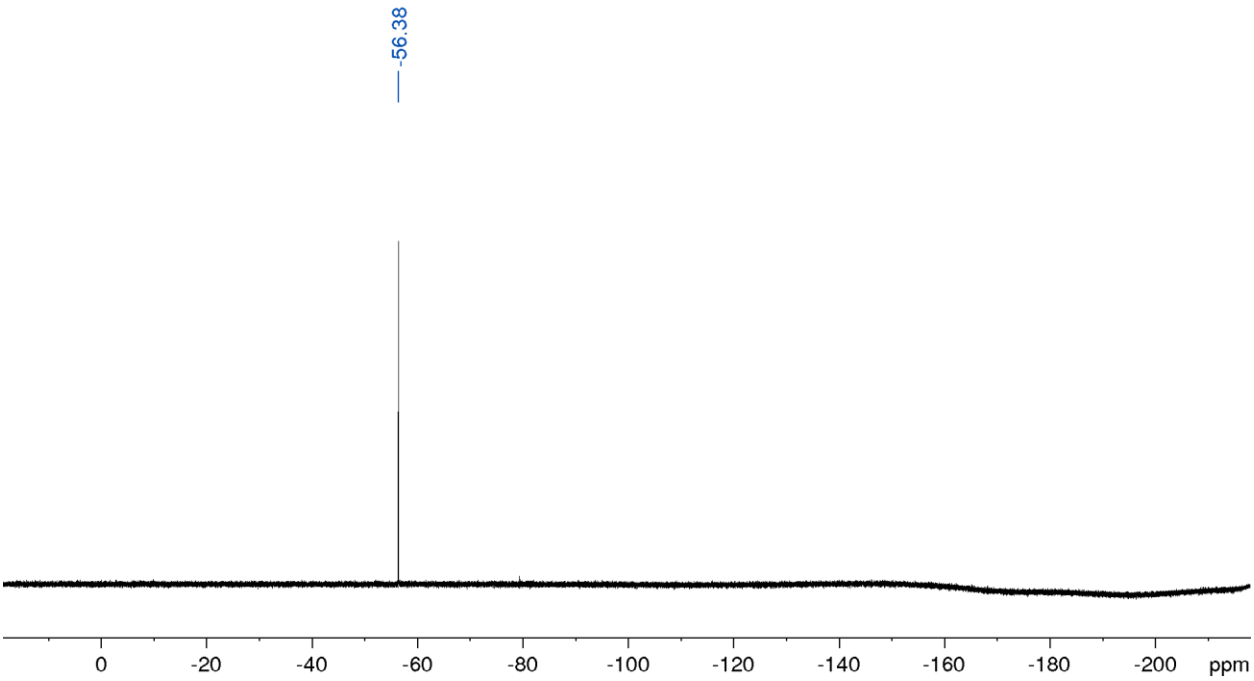

$^{1}$H NMR (700 MHz, MeOD) of **3r**



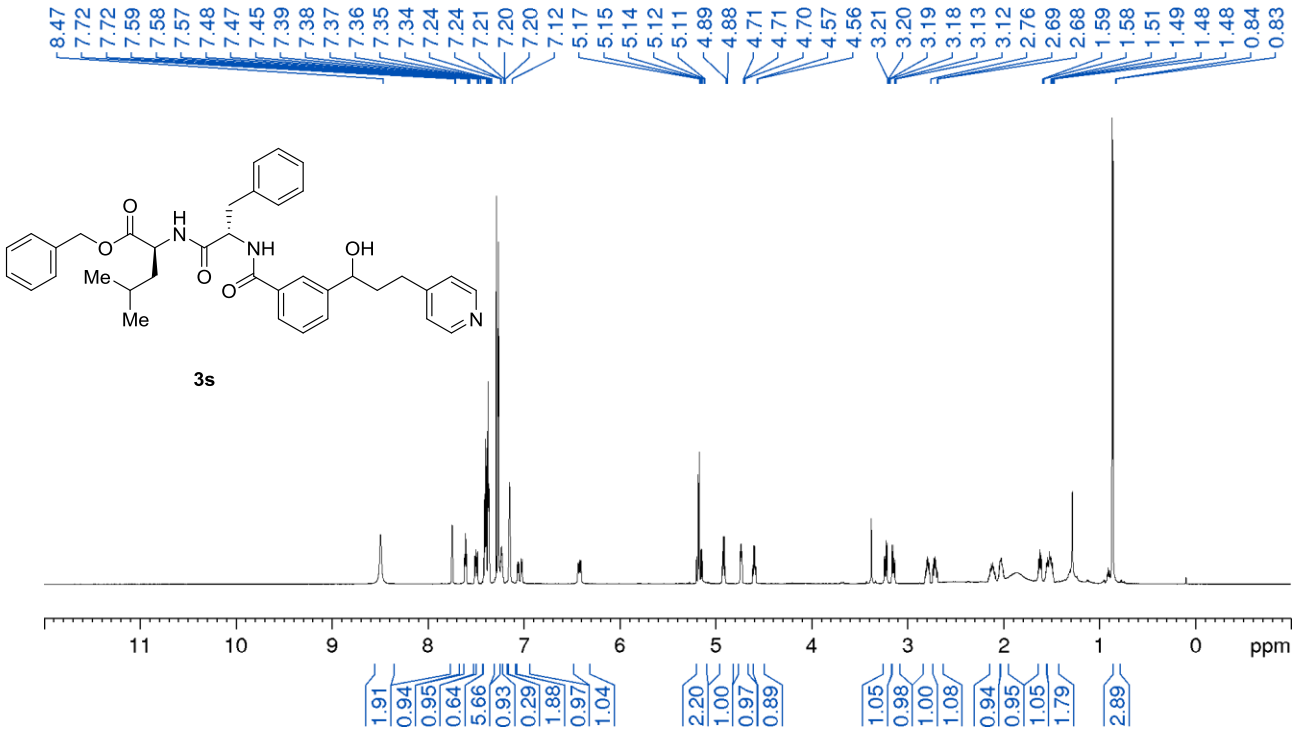
$^{13}$C NMR (176 MHz, MeOD) of **3r**



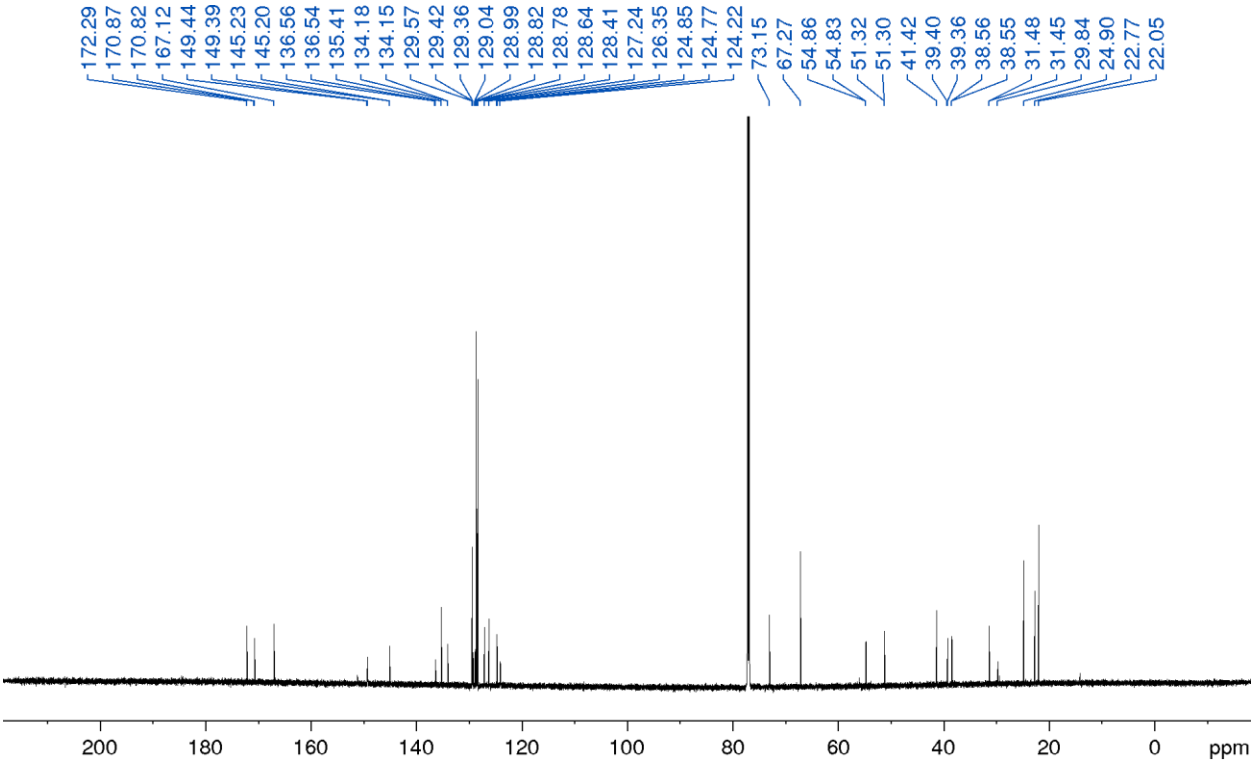

$^{19}$F NMR (376 MHz, MeOD) of **3r**



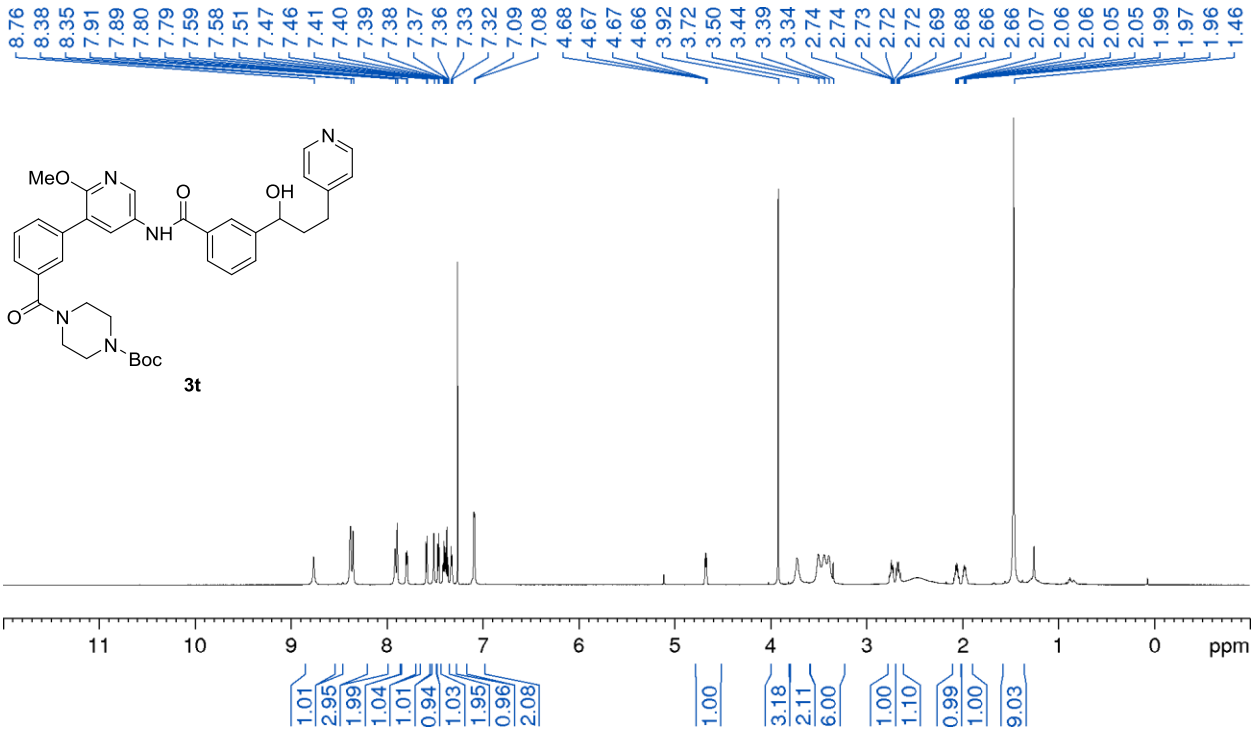
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3s**



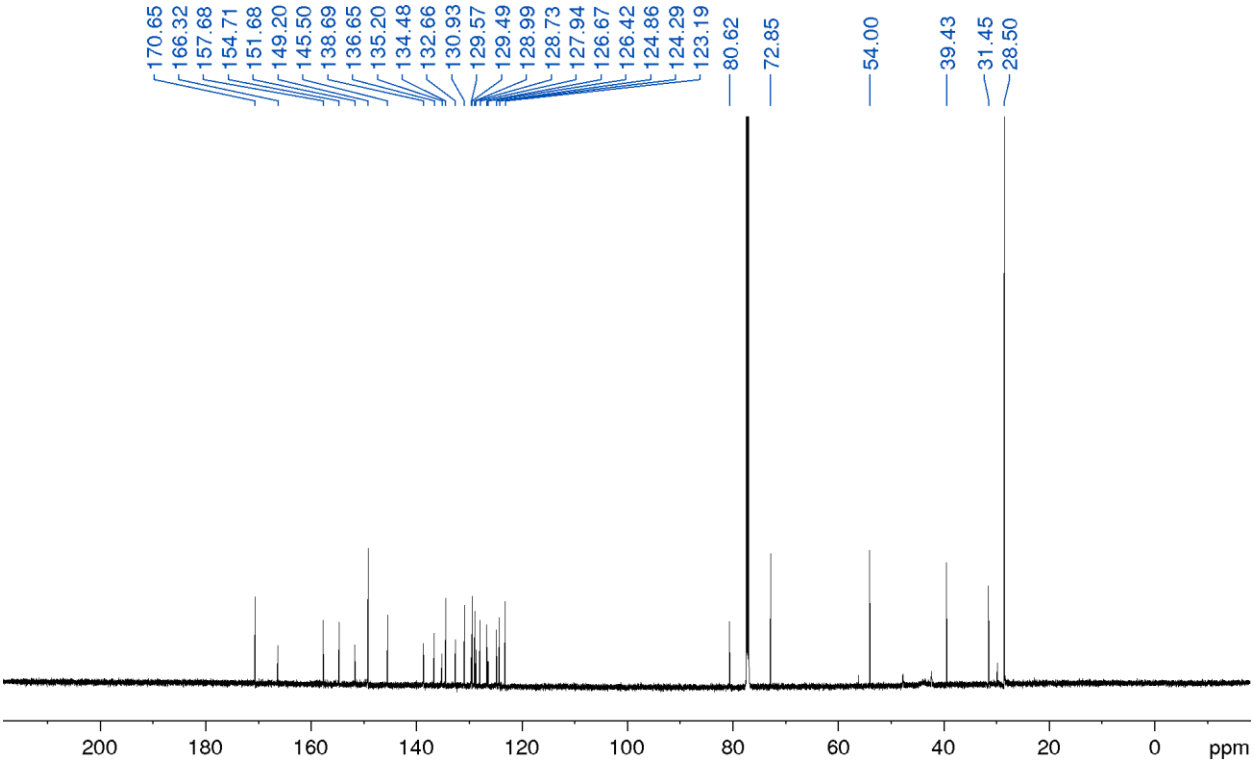

$^{13}$C NMR (176 MHz, $CDCl_3$) of **3s**



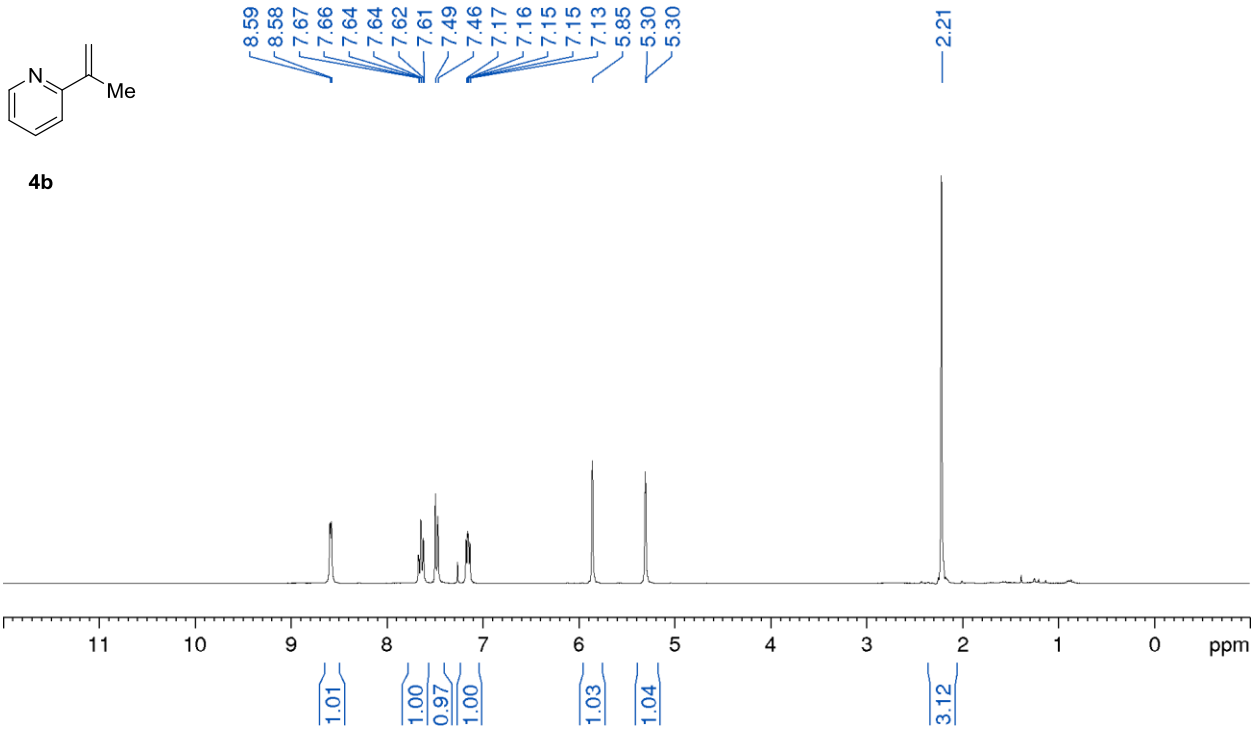
$^{1}$H NMR (700 MHz, $CDCl_3$) of **3t**



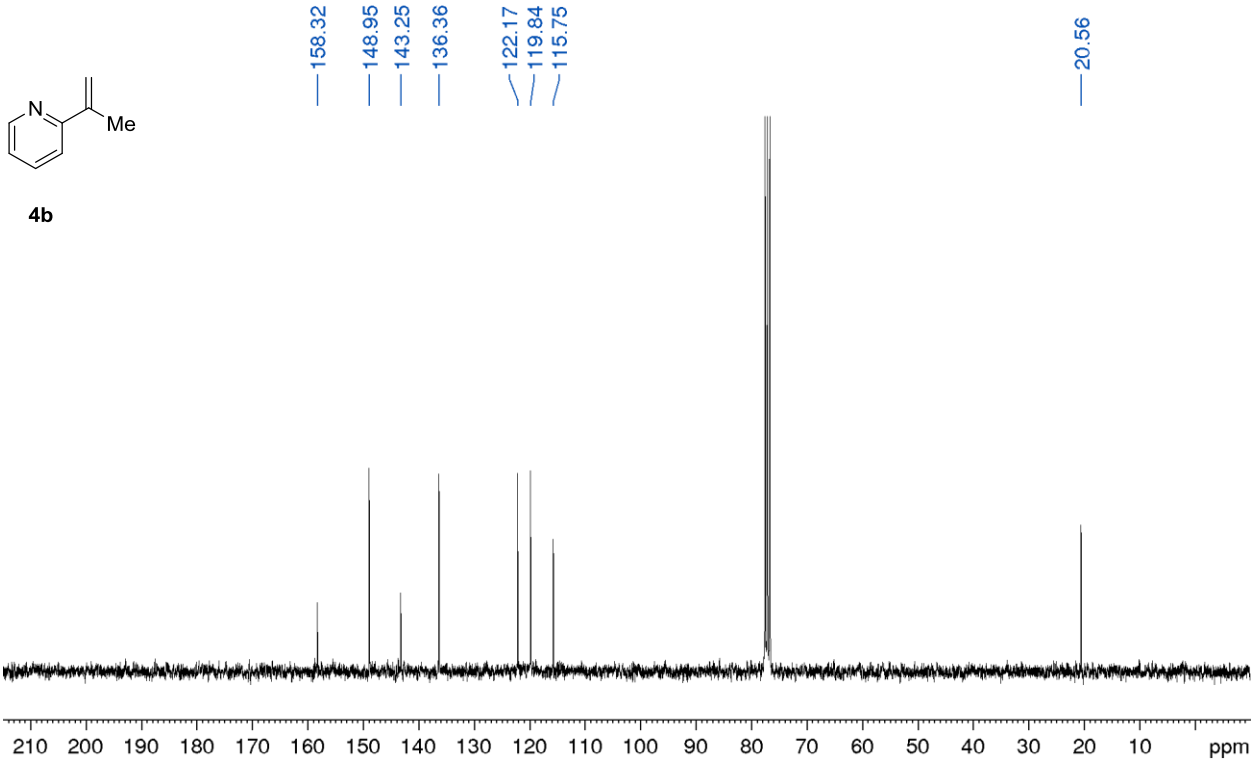

$^{13}$C NMR (176 MHz, $CDCl_3$) of **3t**



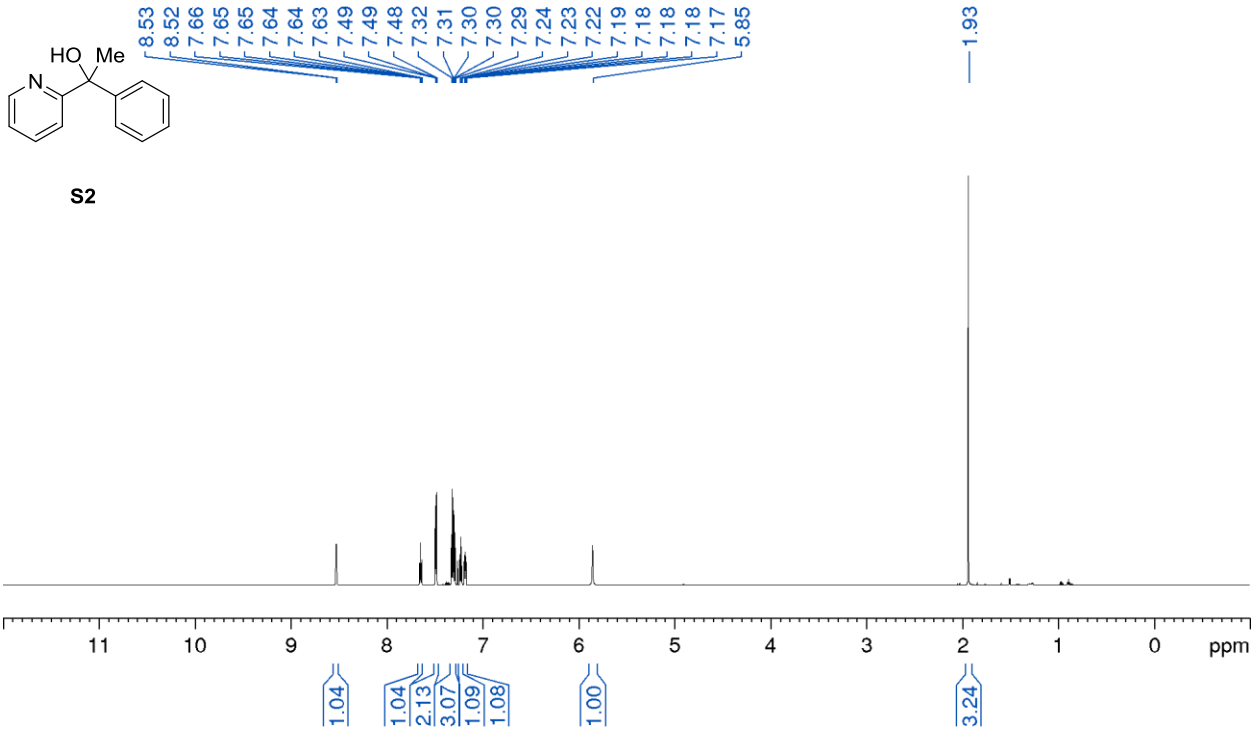
$^{1}$H NMR (300 MHz, $CDCl_3$, 25 ºC) of **4b**



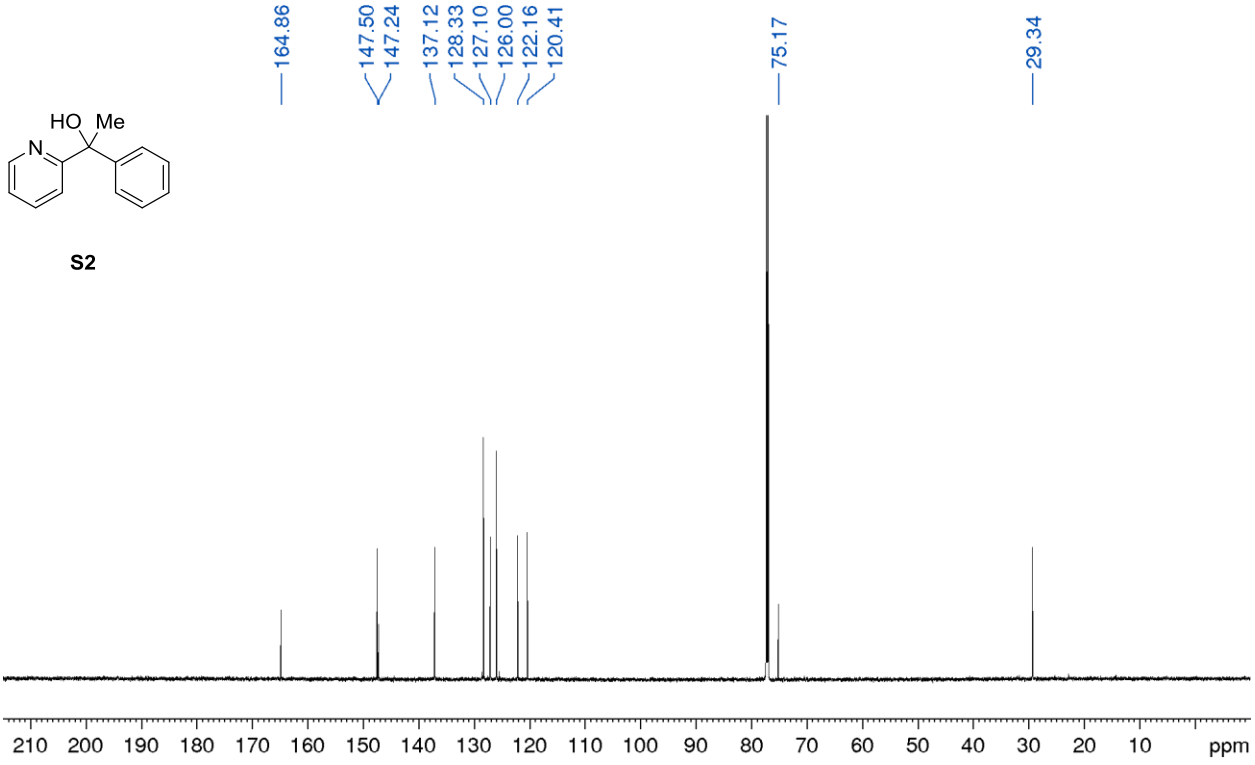

$^{13}$C NMR (75 MHz, $CDCl_3$, 25 ºC) of **4b**



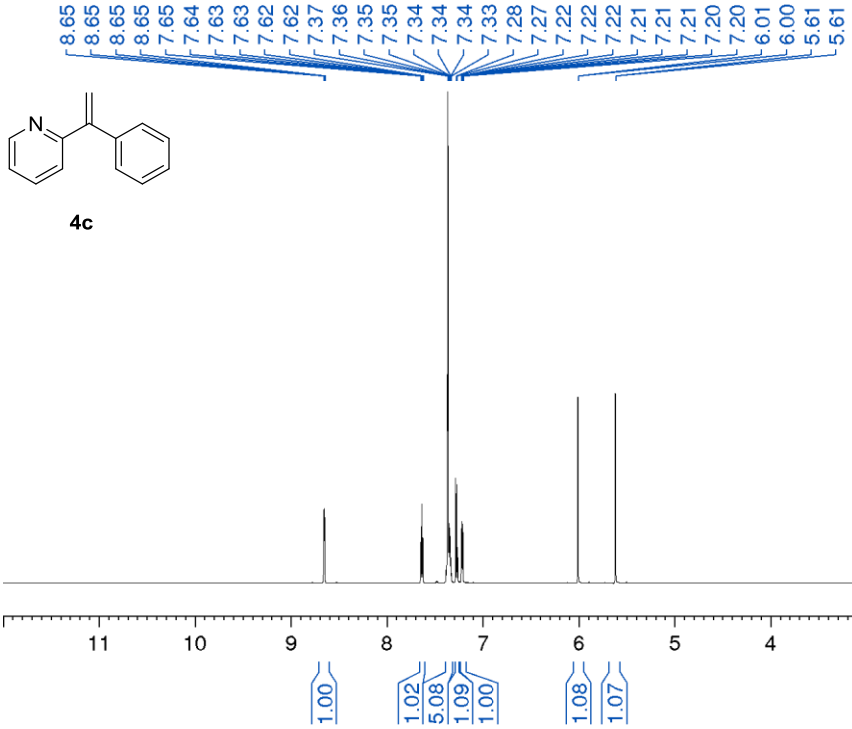
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S2**



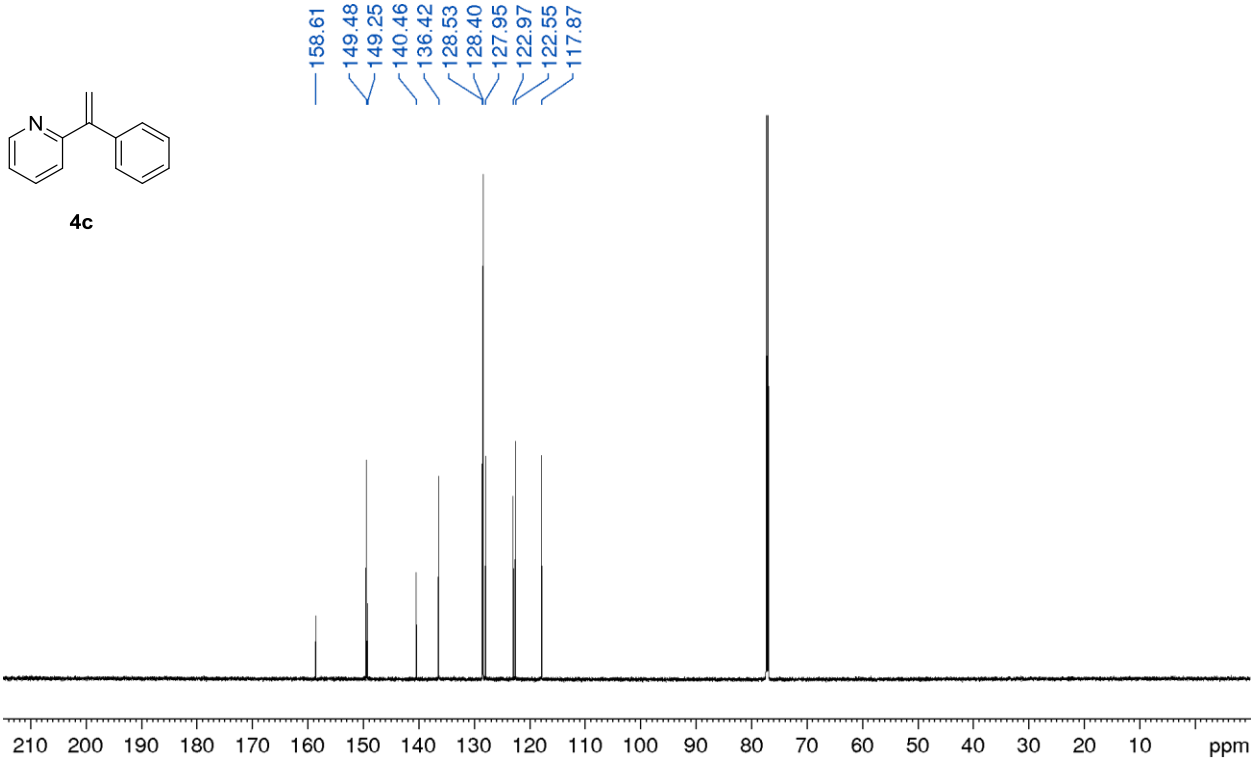

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S2**



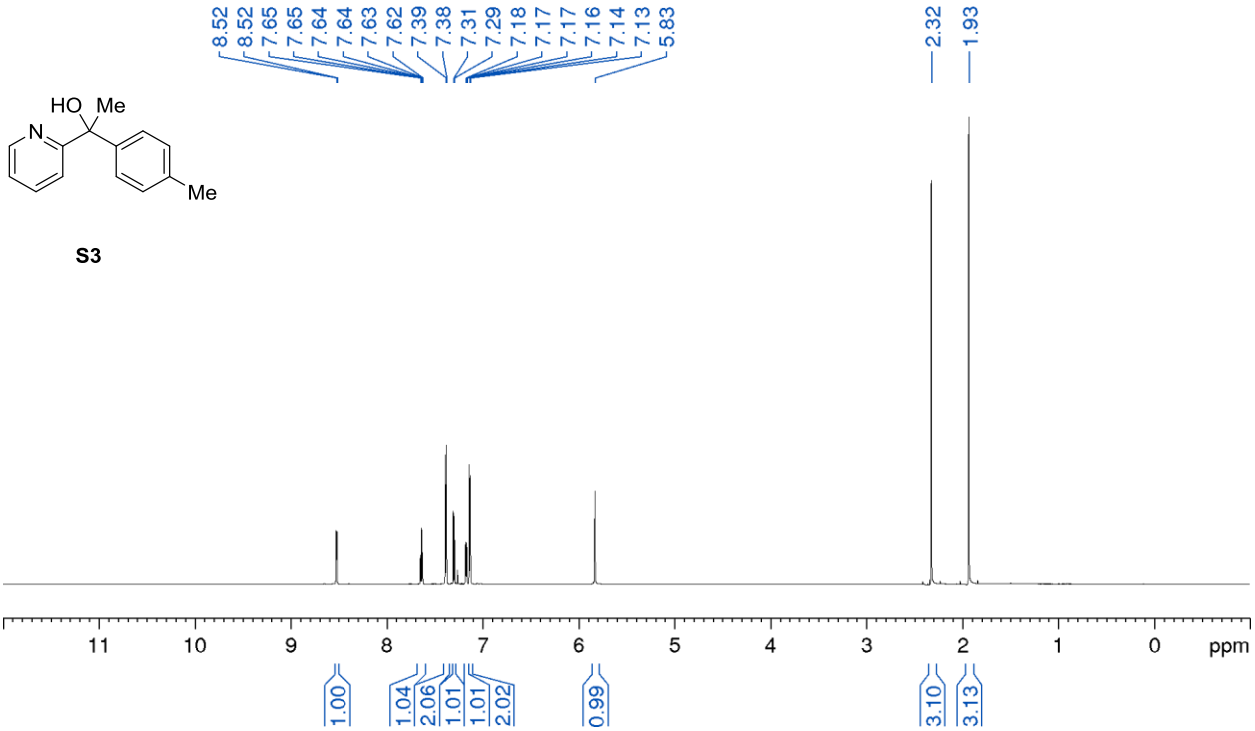
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4c**



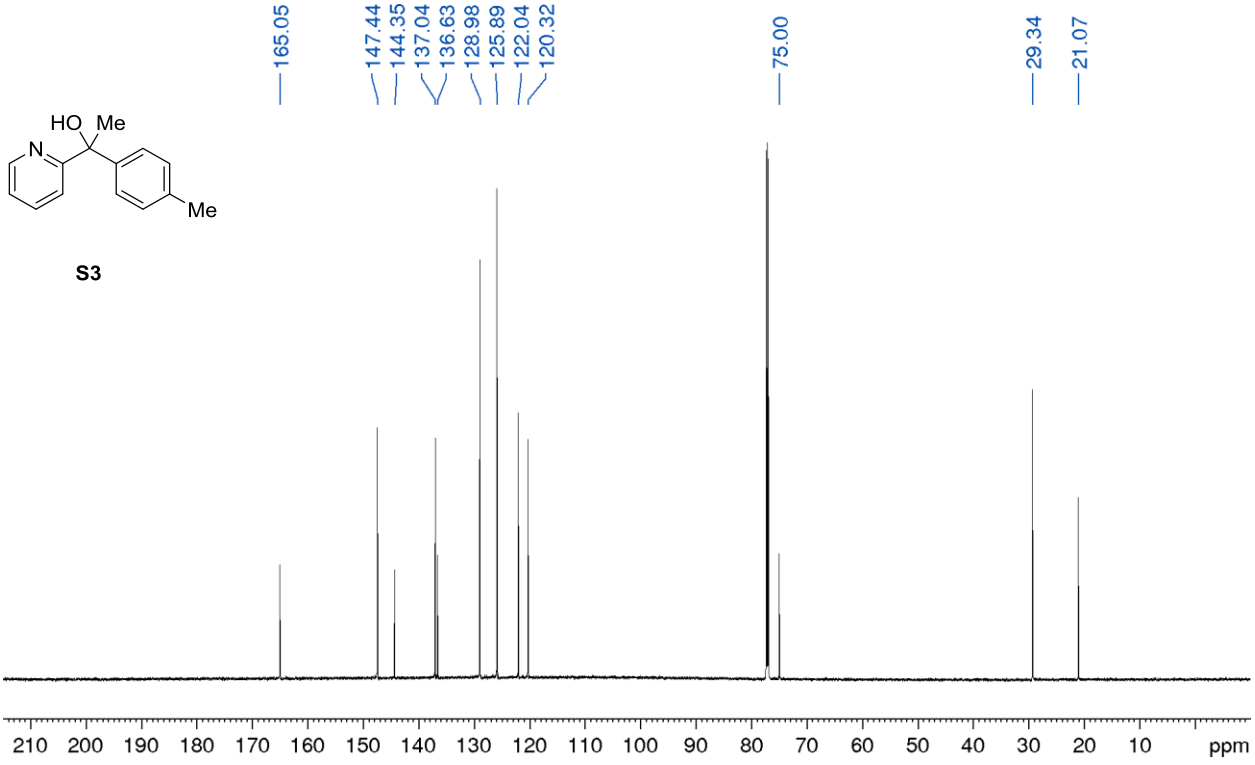

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4c**



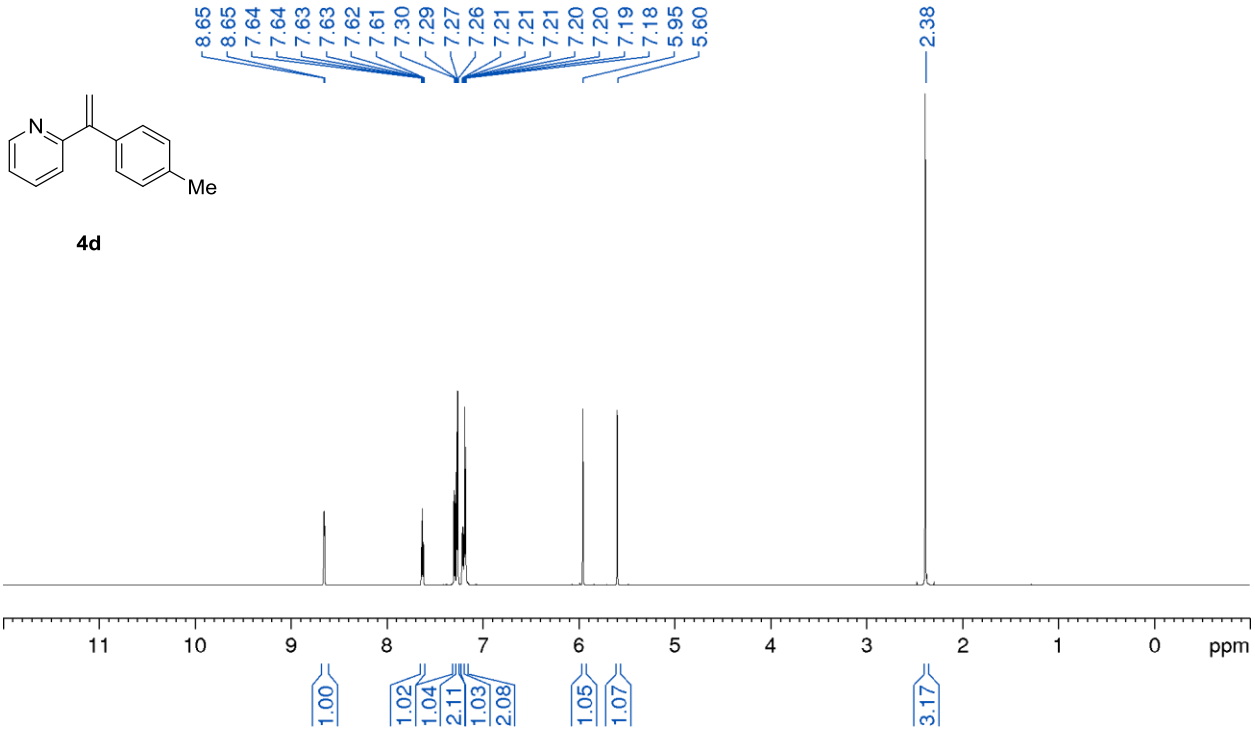
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S3**



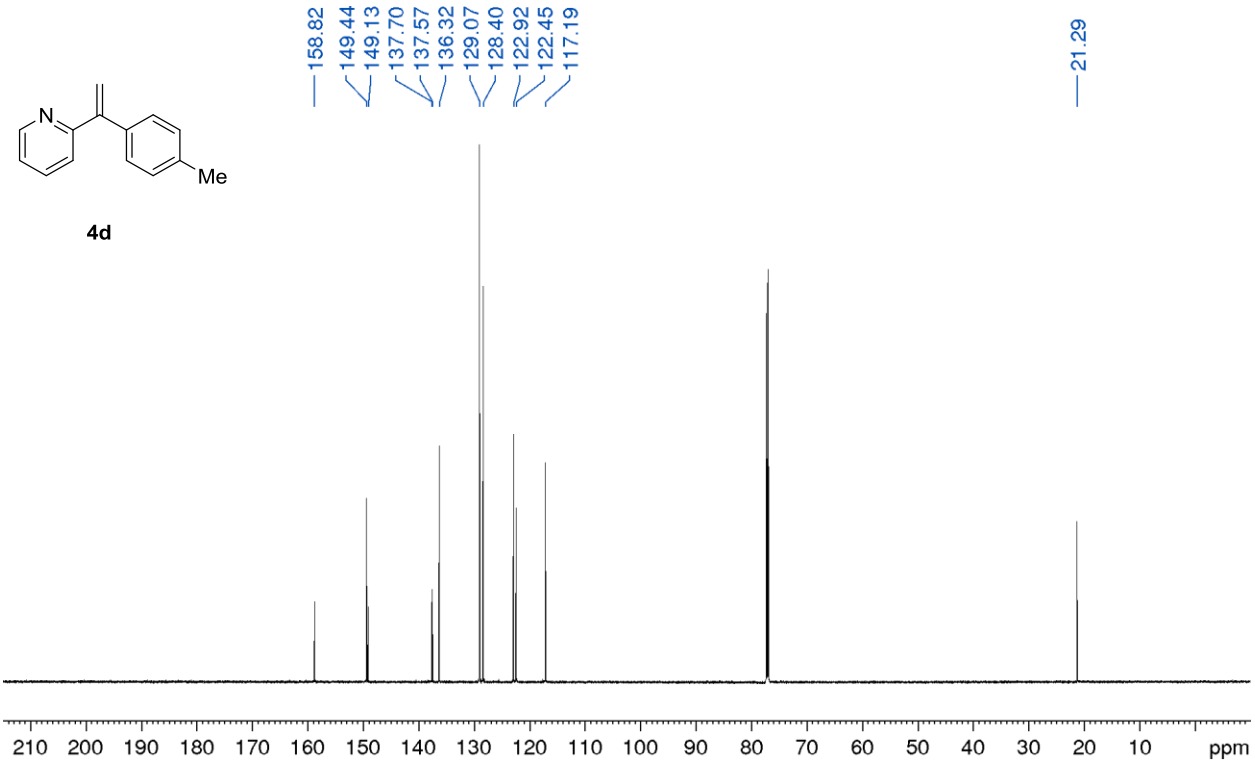

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S3**



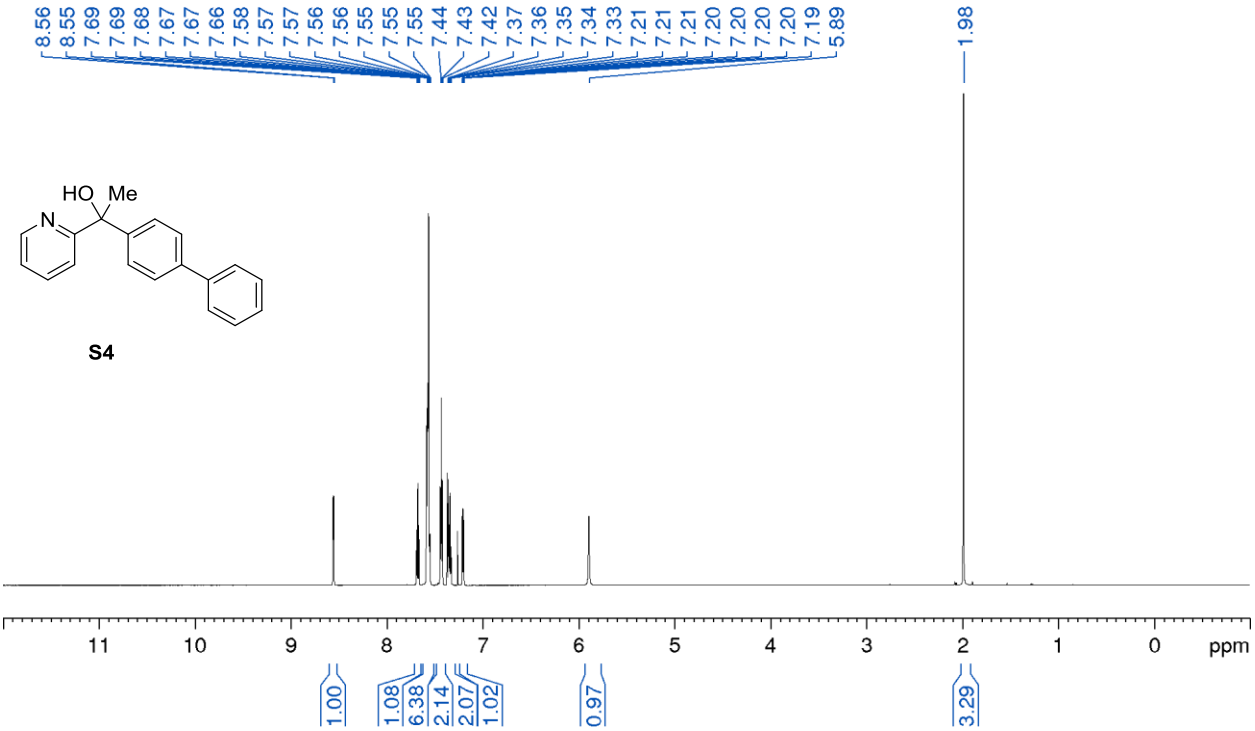
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4d**



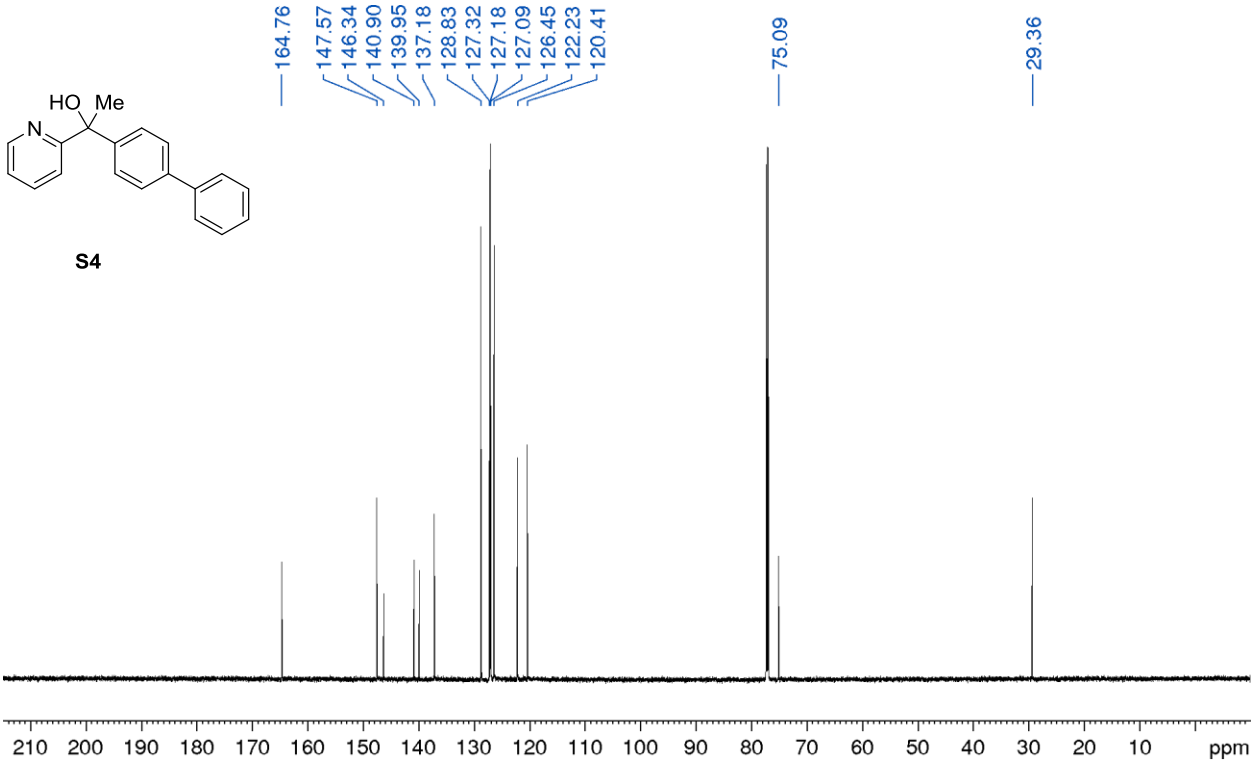

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4d**



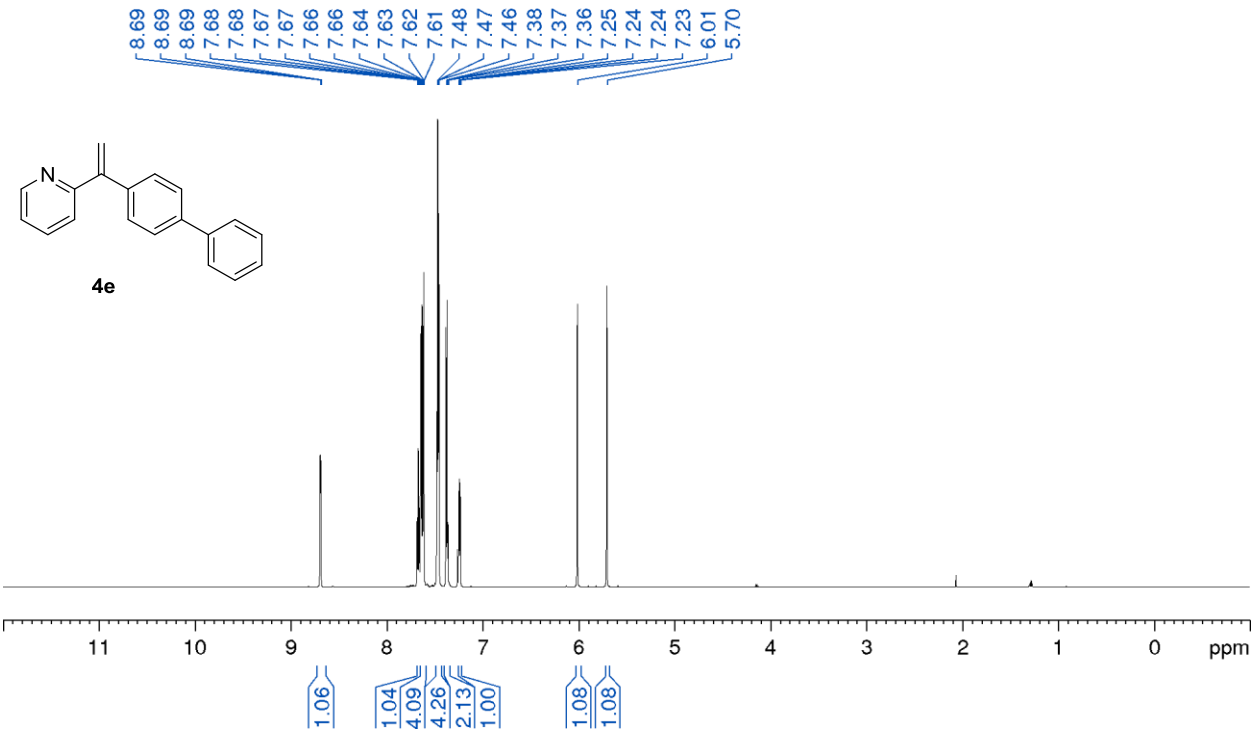
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S4**



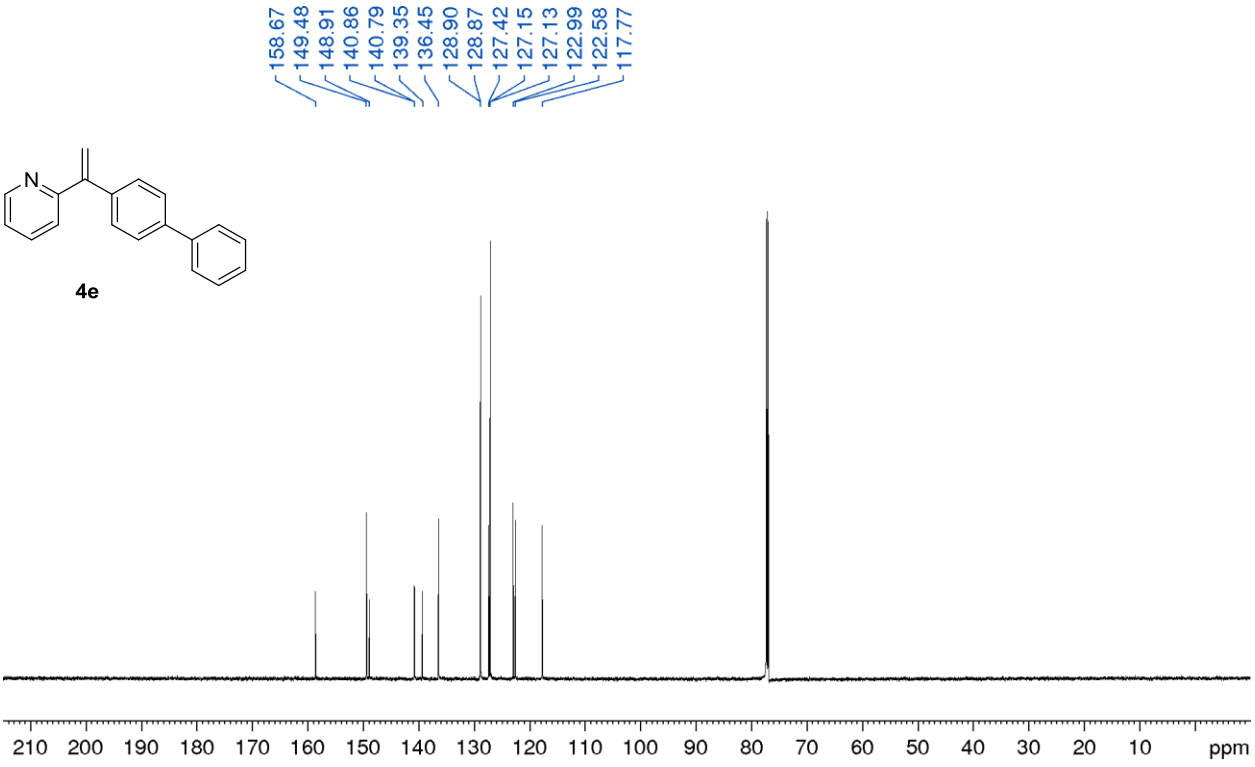

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S4**



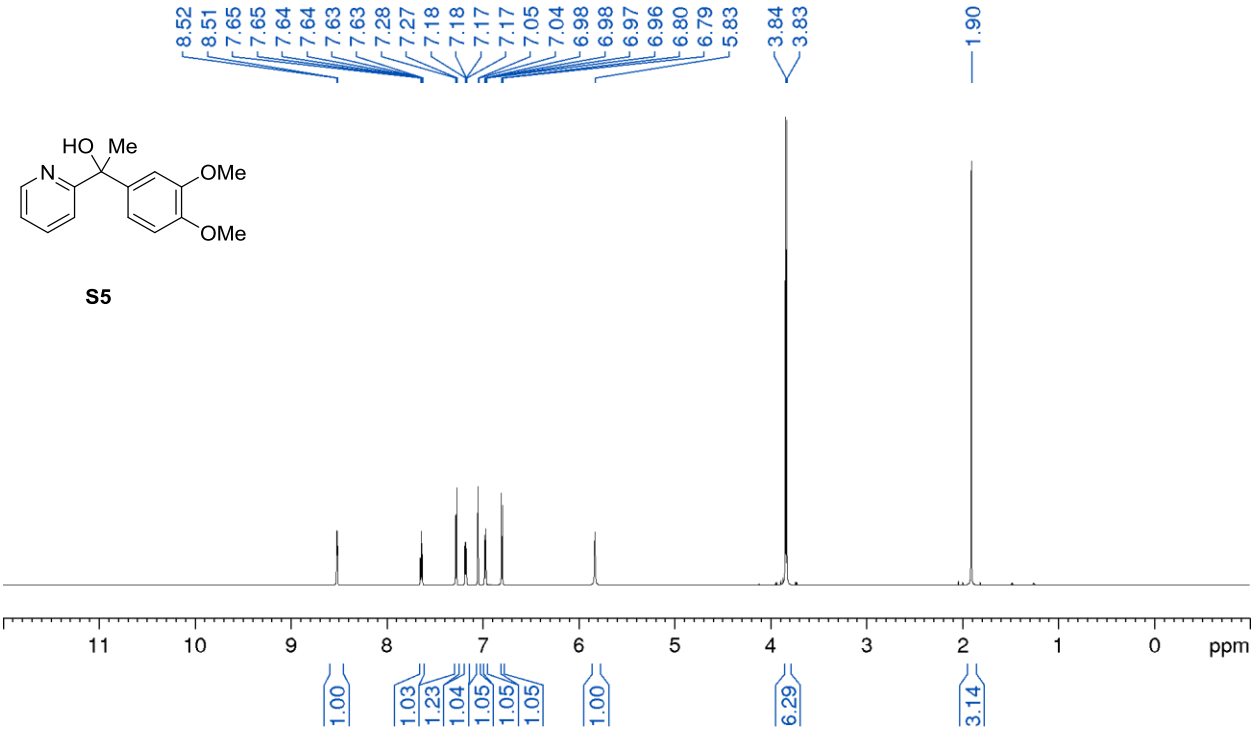
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4e**



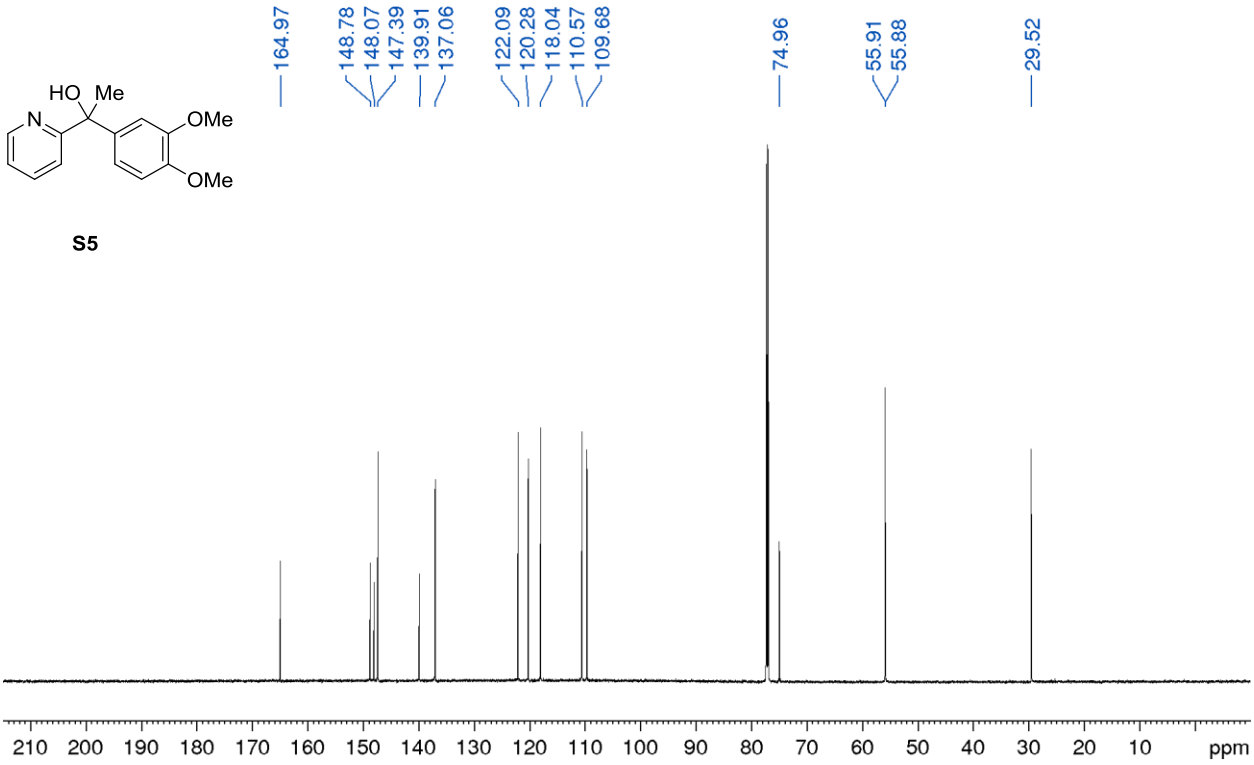

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4e**



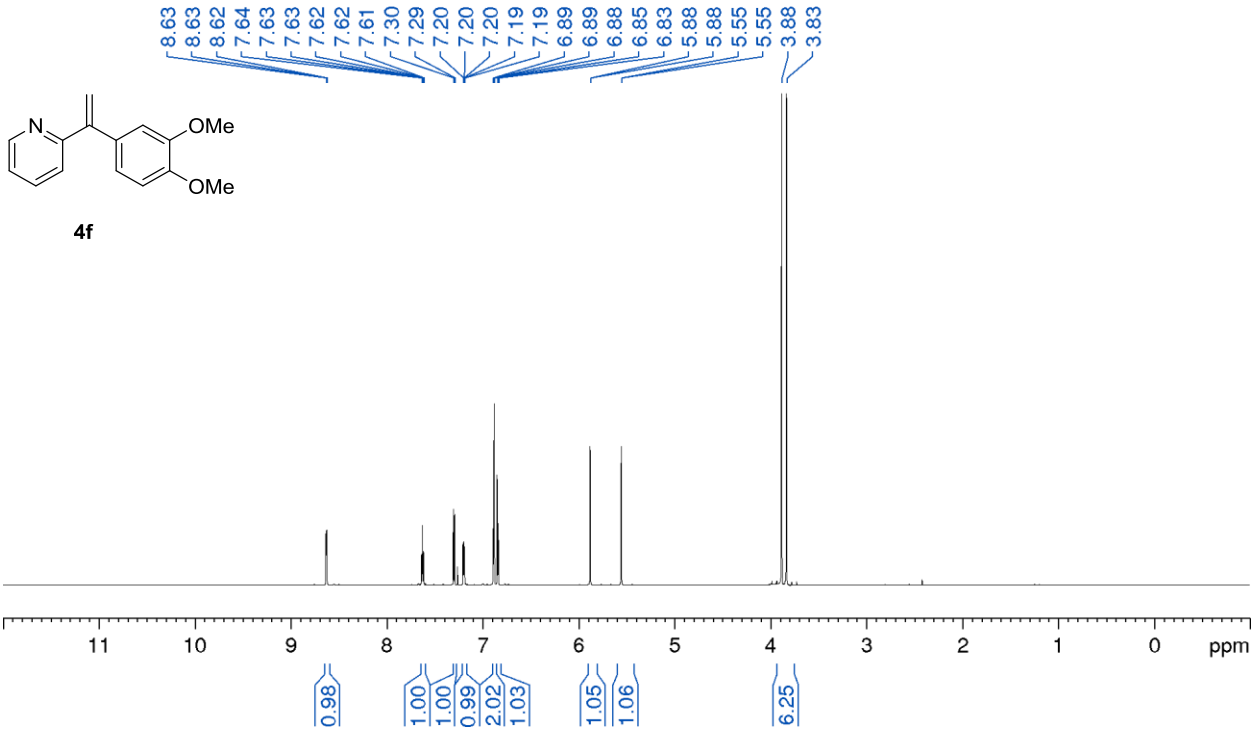
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S5**



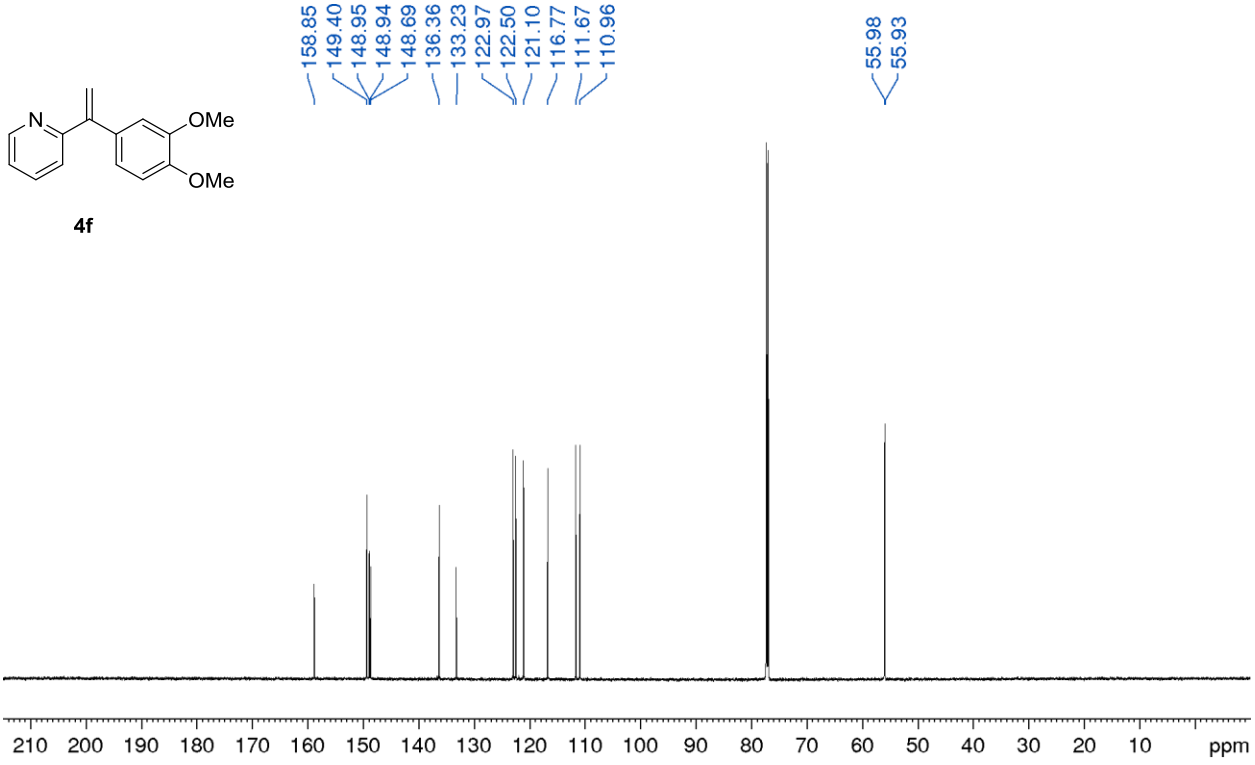

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S5**



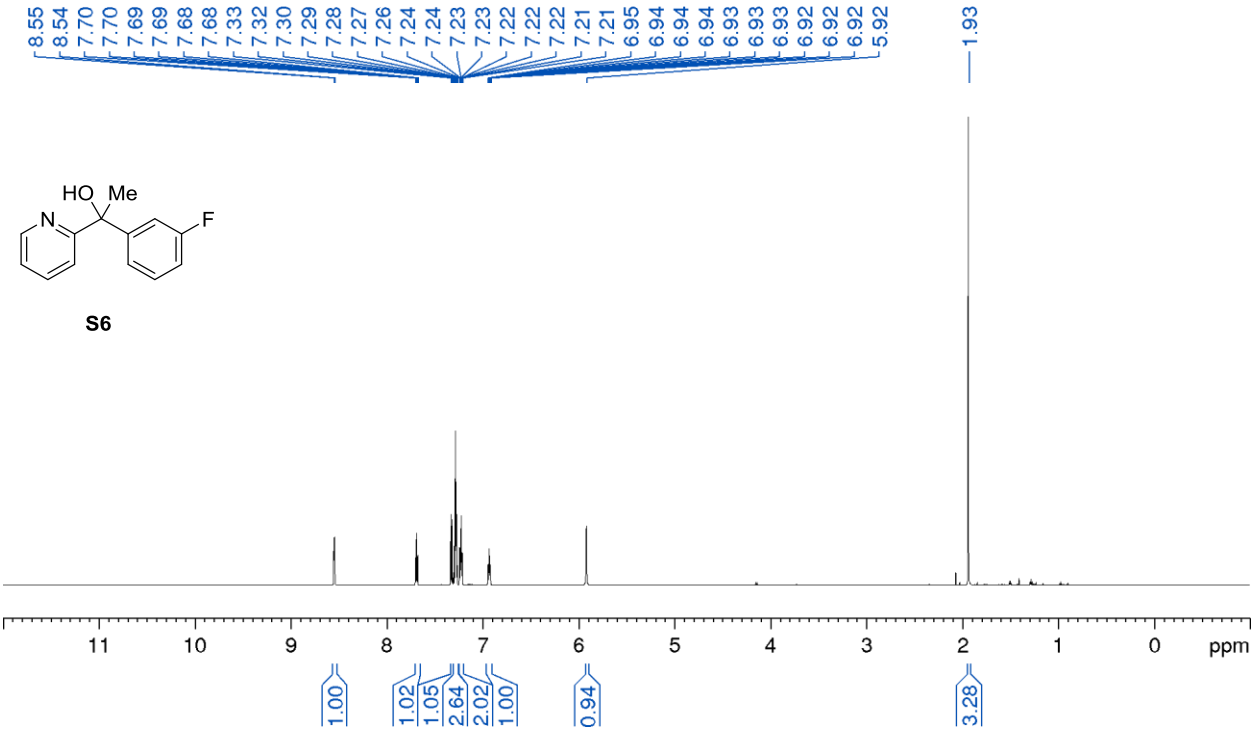
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4f**




$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4f**

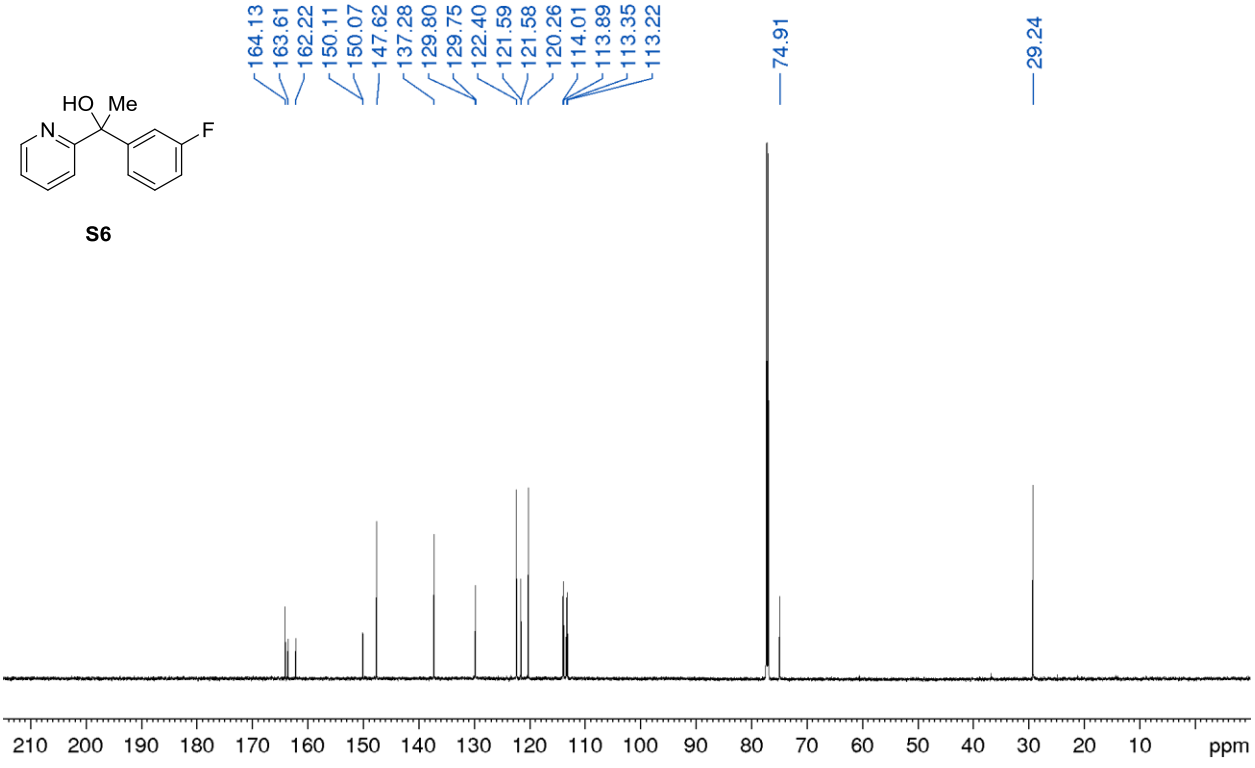


$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S6**



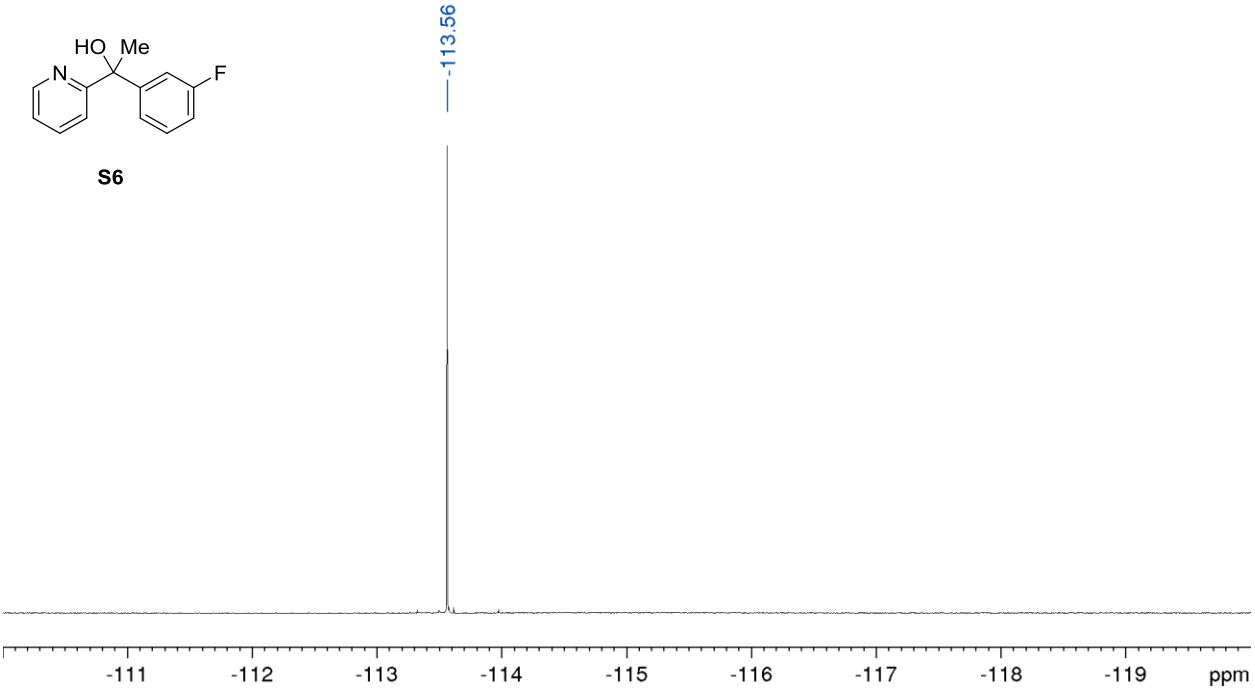

**S6**

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S6**

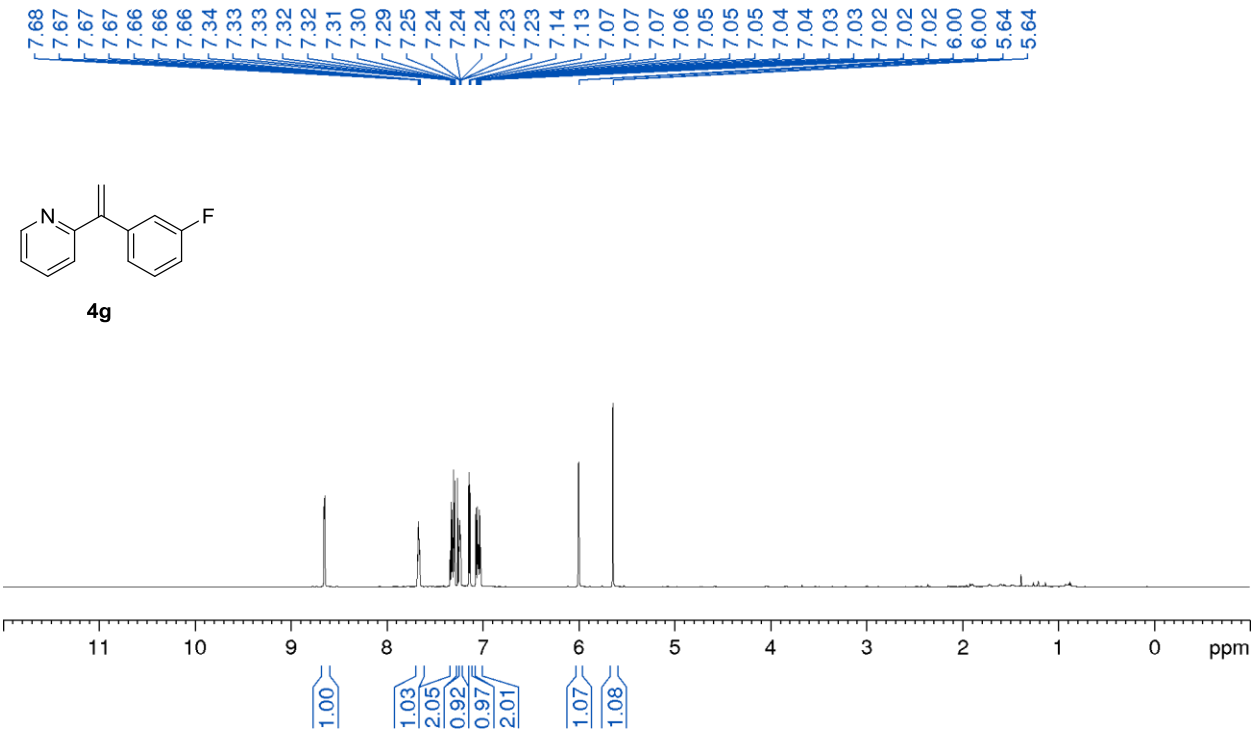



**S6**

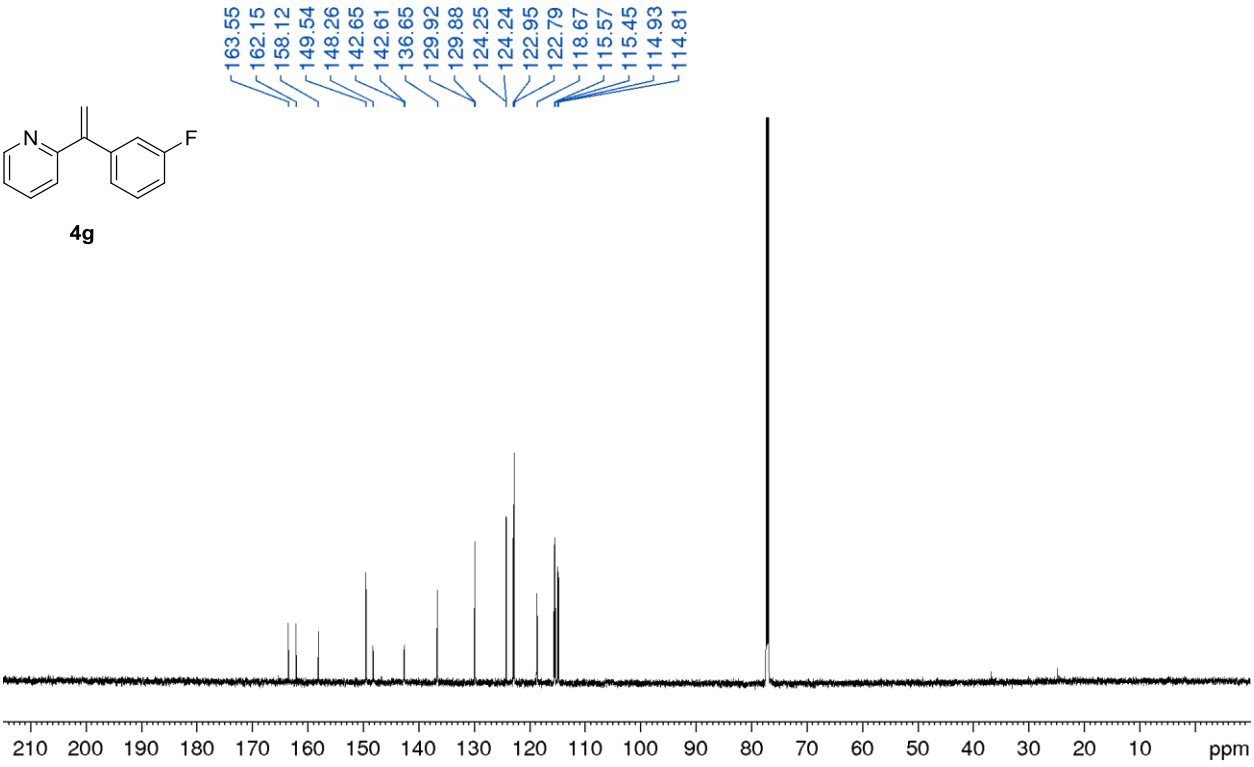
$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **S6**



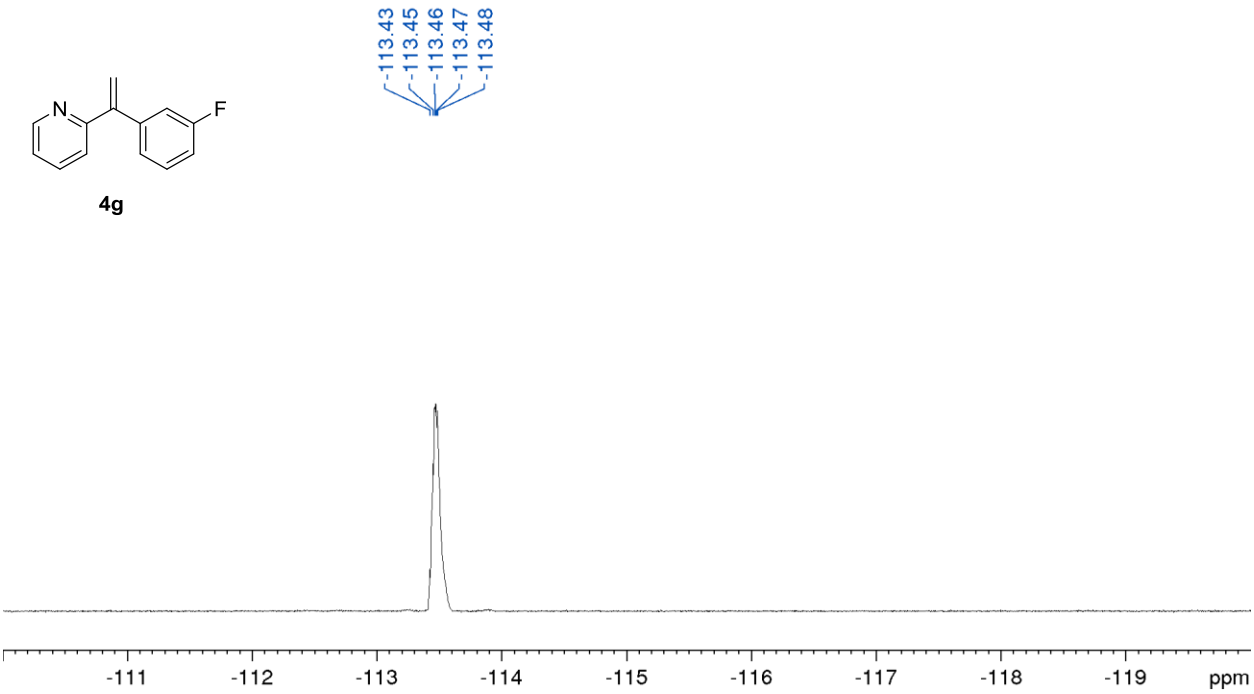

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4g**



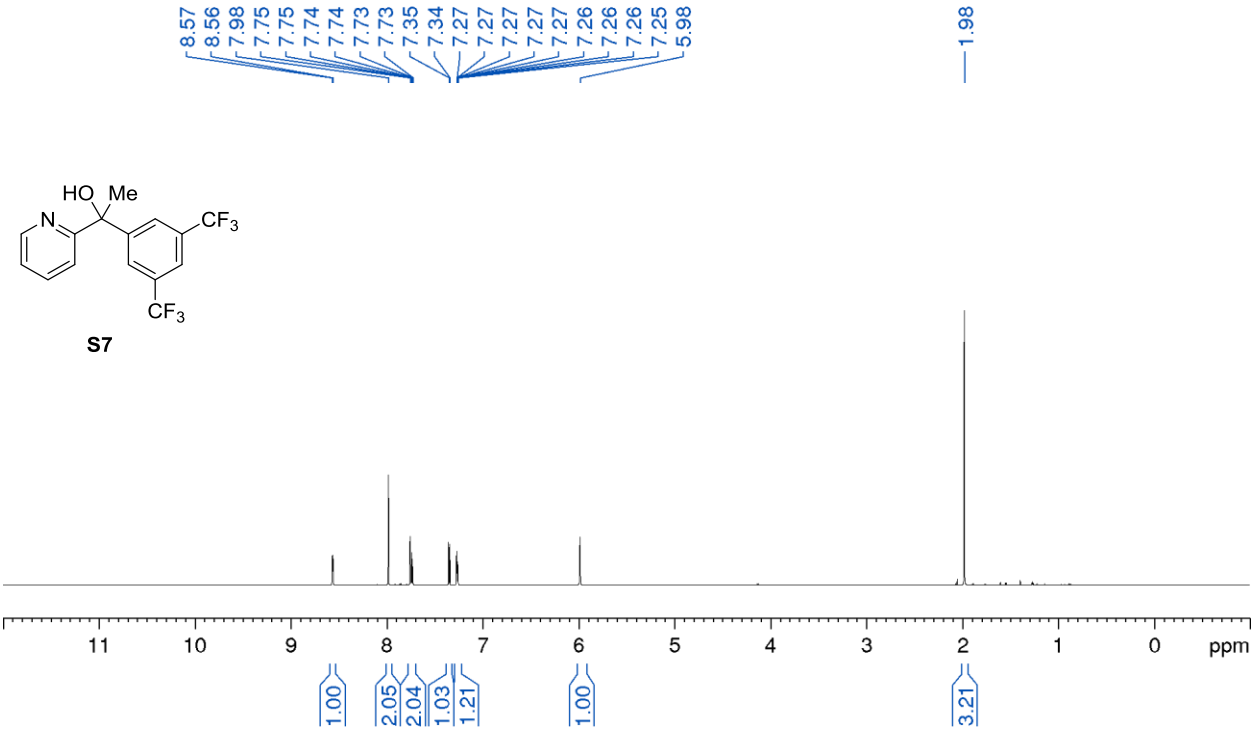
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4g**



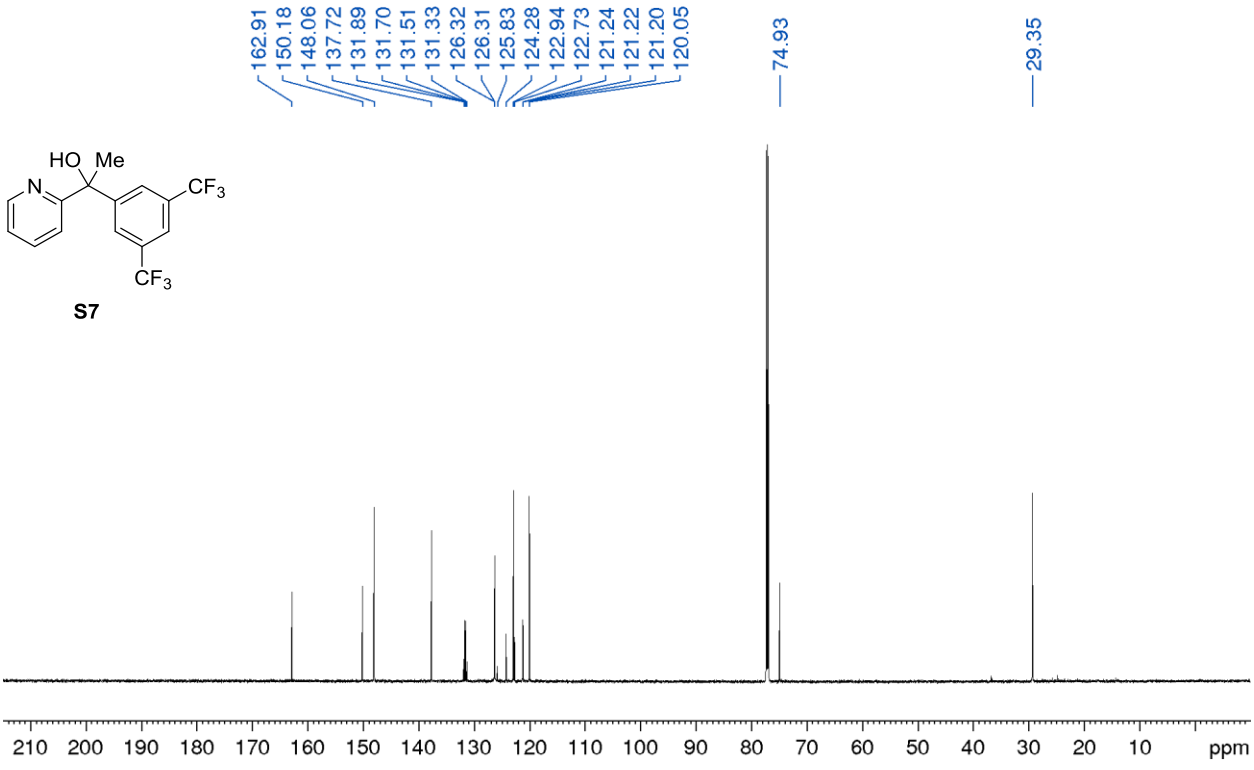

$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **4g**



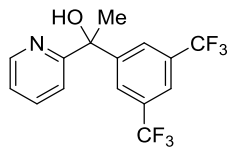
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S7**




$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S7**



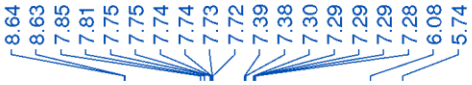
$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **S7**

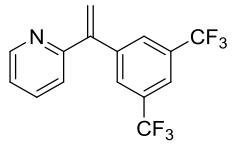



**S7**

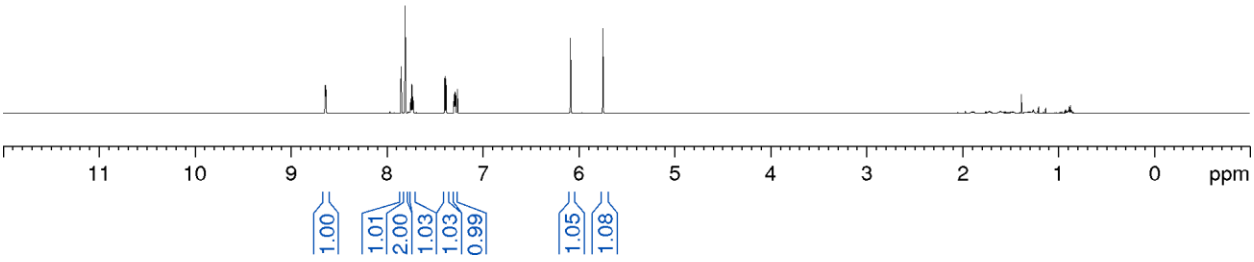



$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4h**

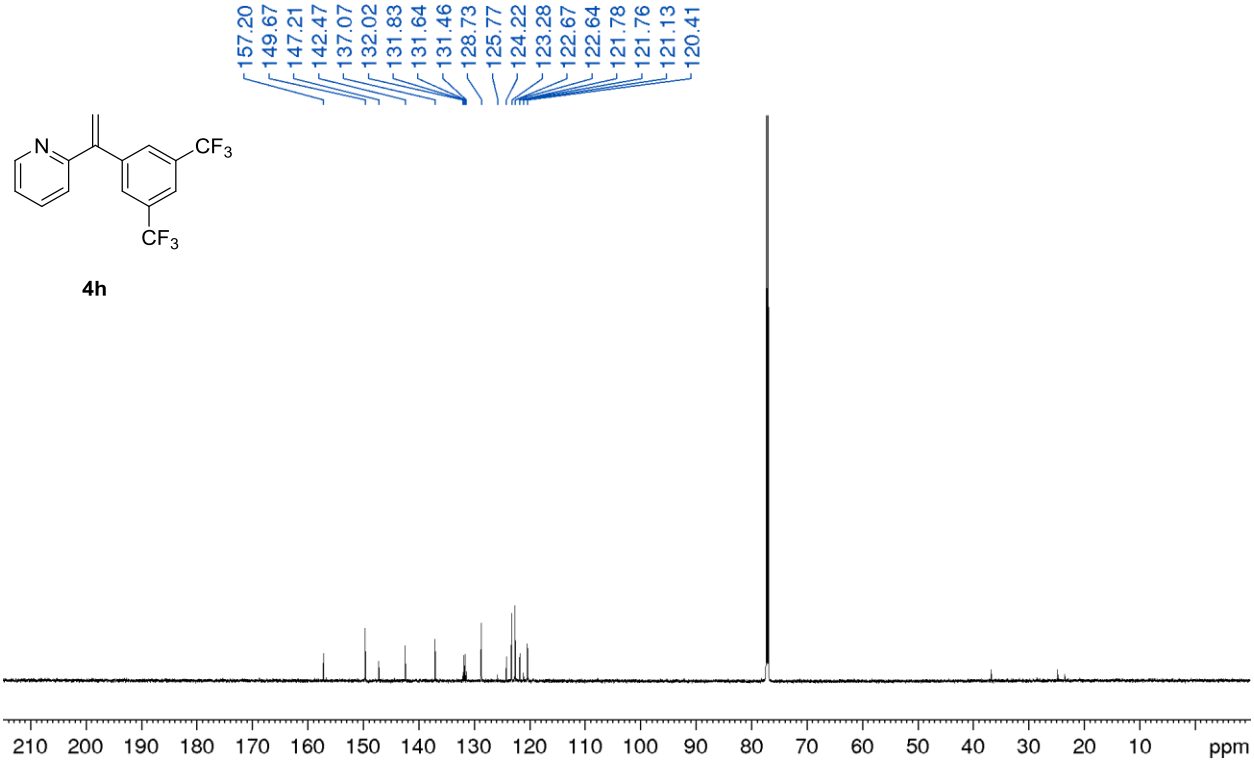


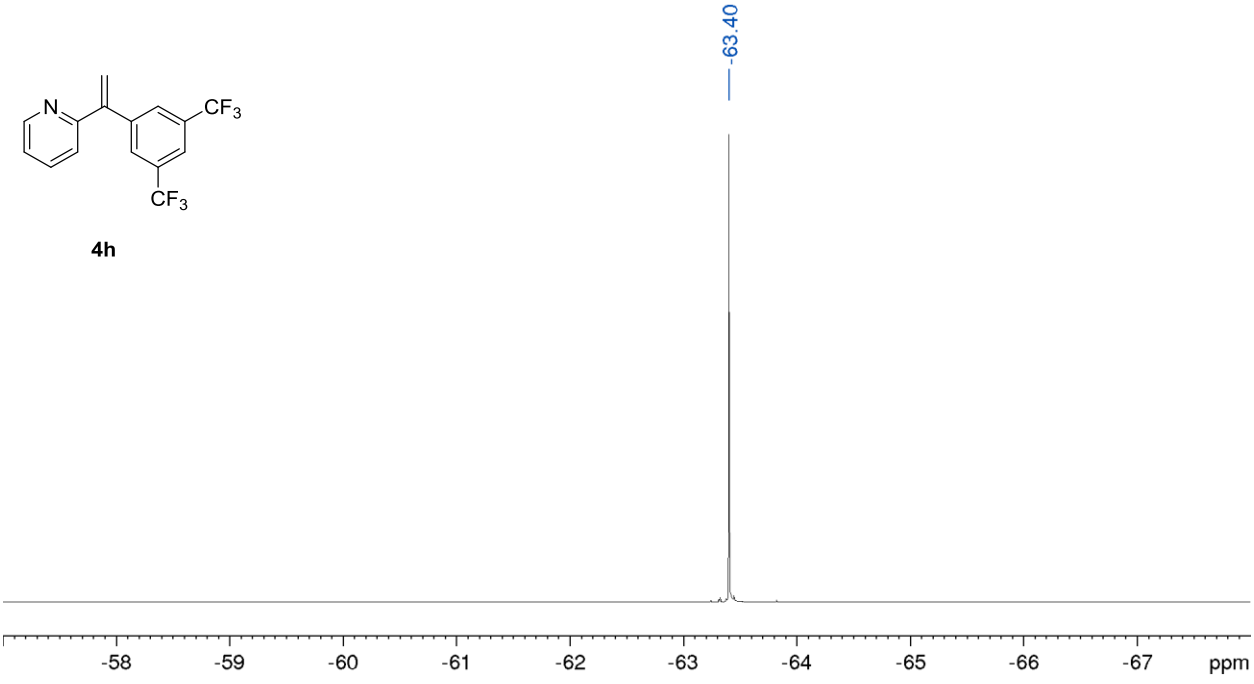

**4h**



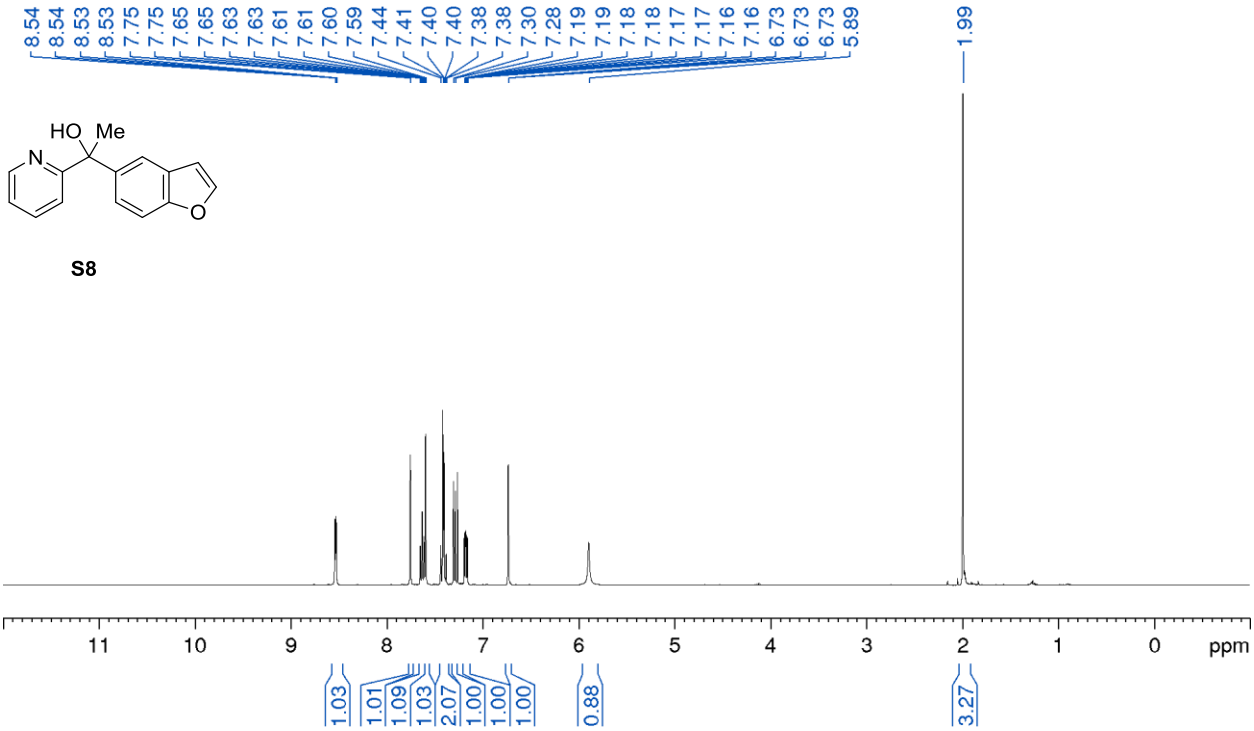
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4h**



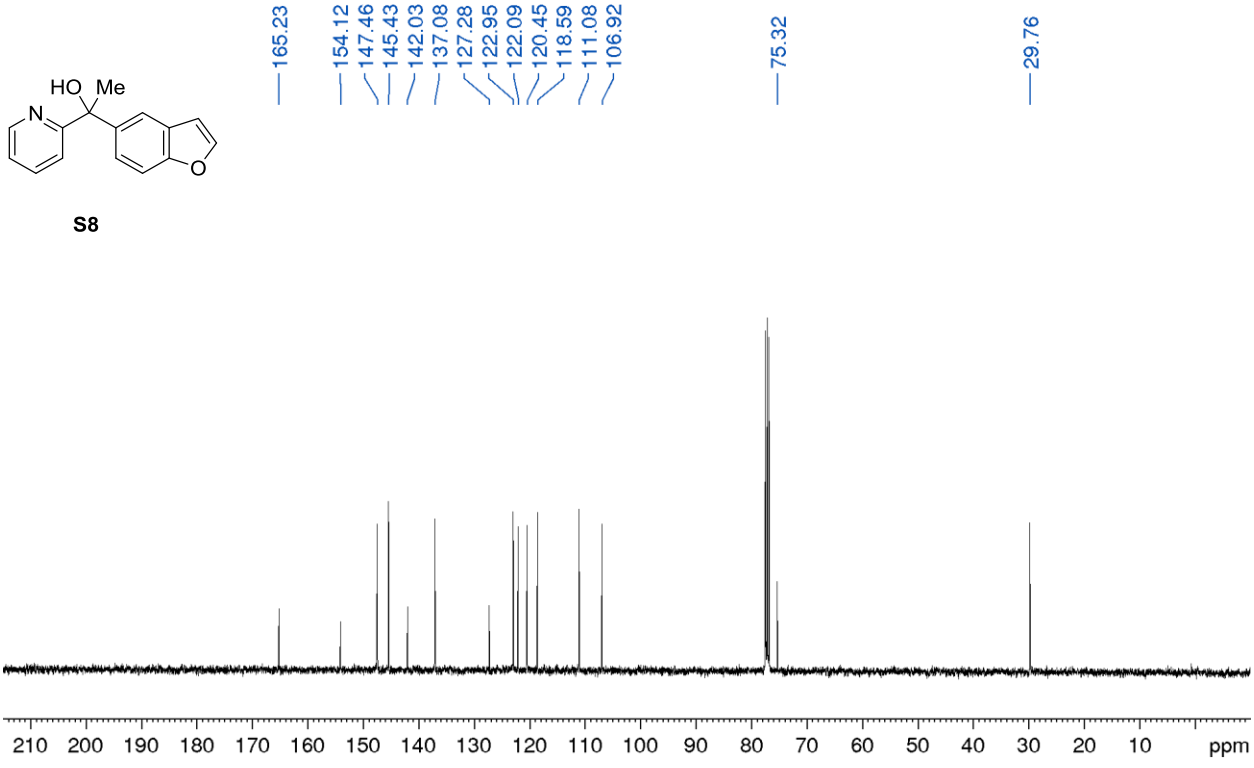

$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **4h**



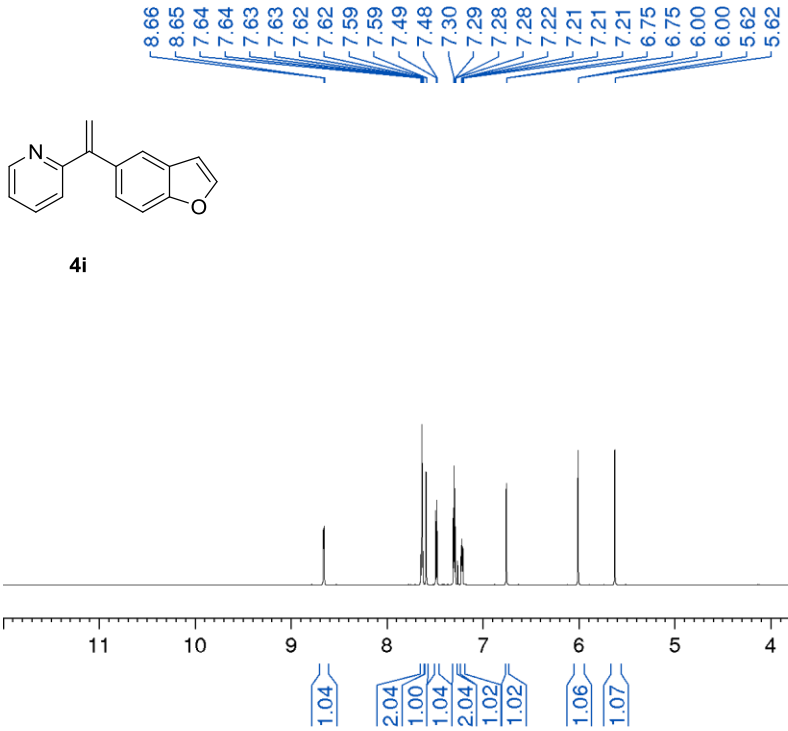
$^{1}$H NMR (400 MHz, $CDCl_3$, 25 ºC) of **S8**



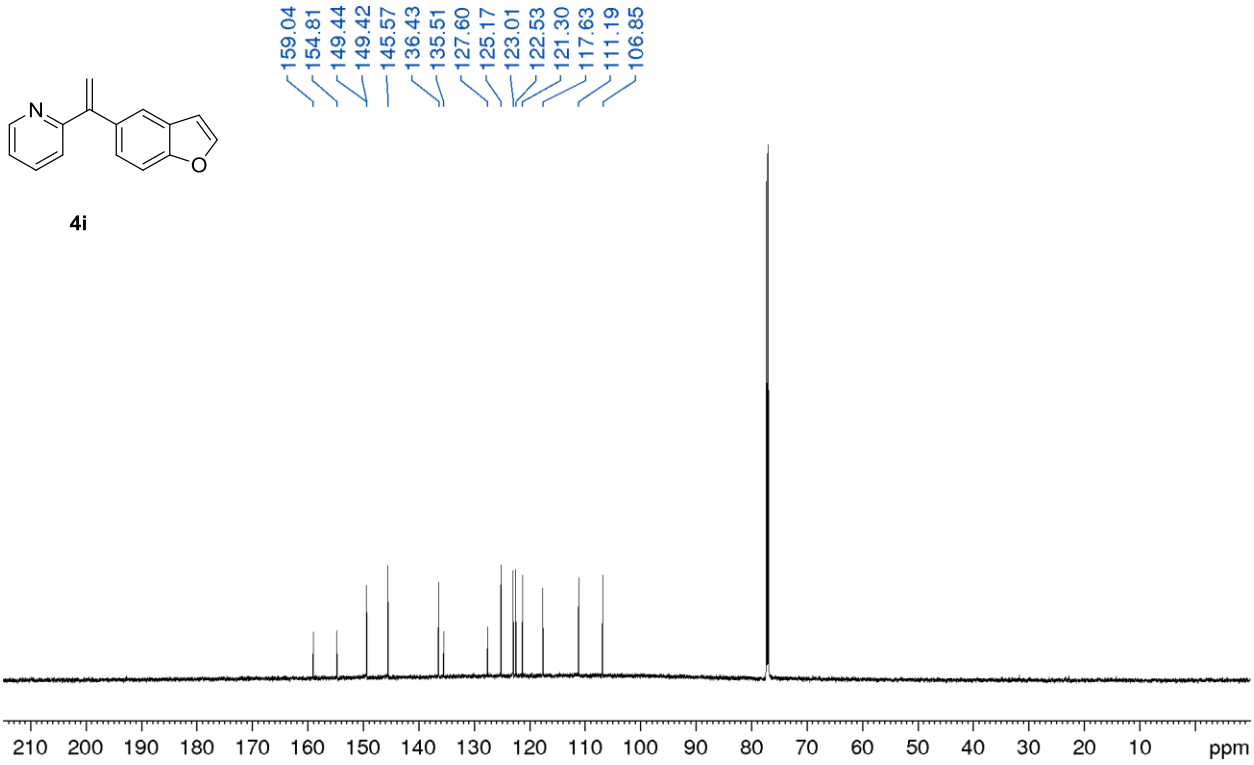

$^{13}$C NMR (100 MHz, $CDCl_3$, 25 ºC) of **S8**



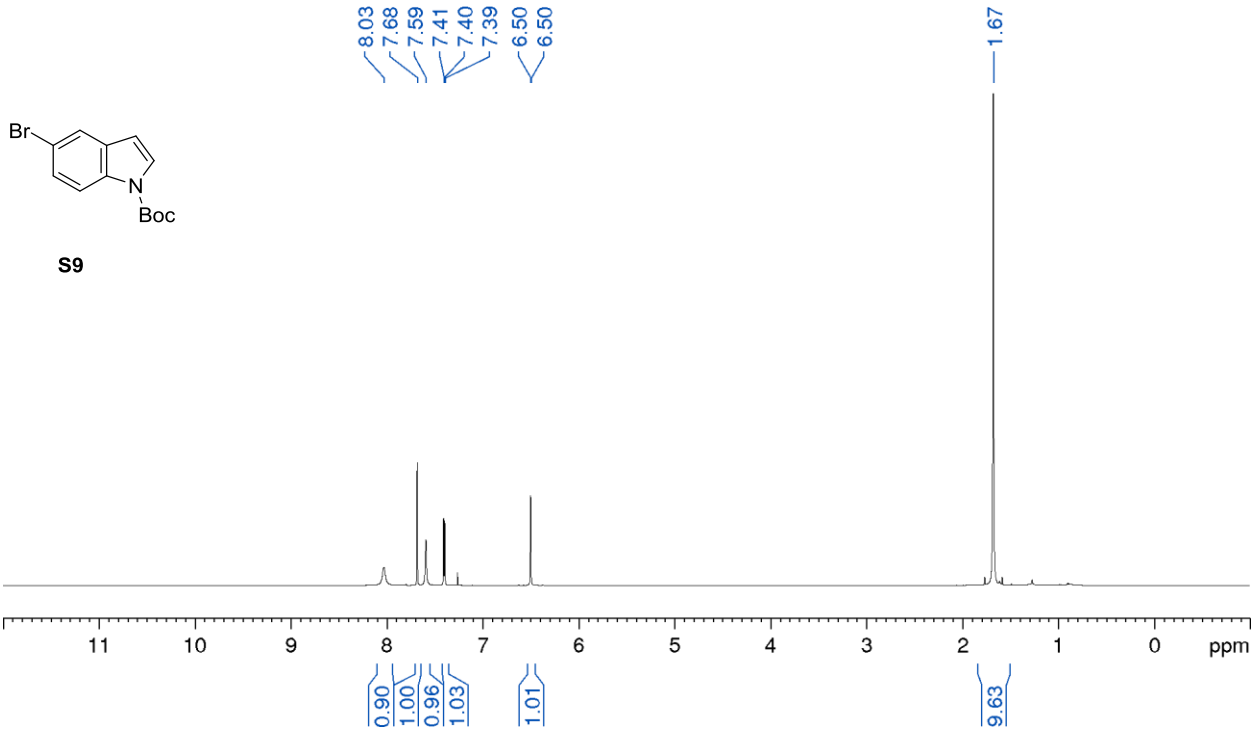
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4i**



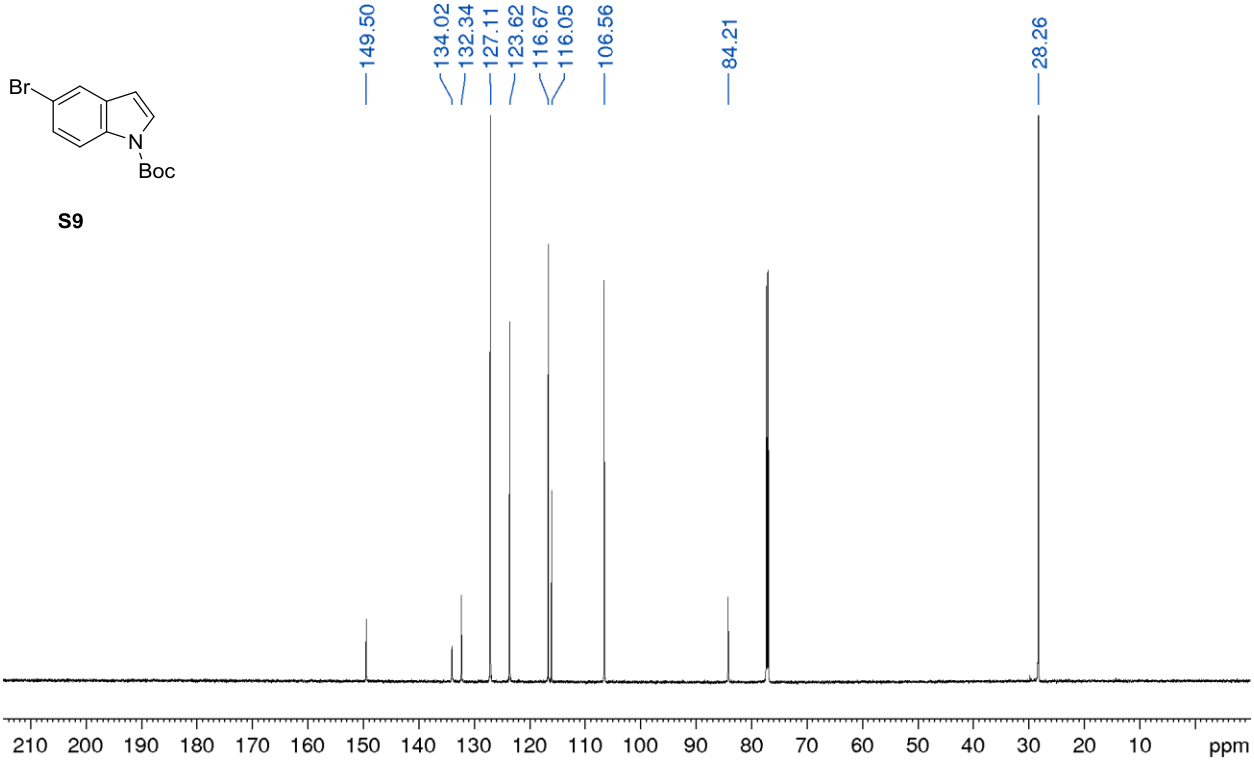

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4i**



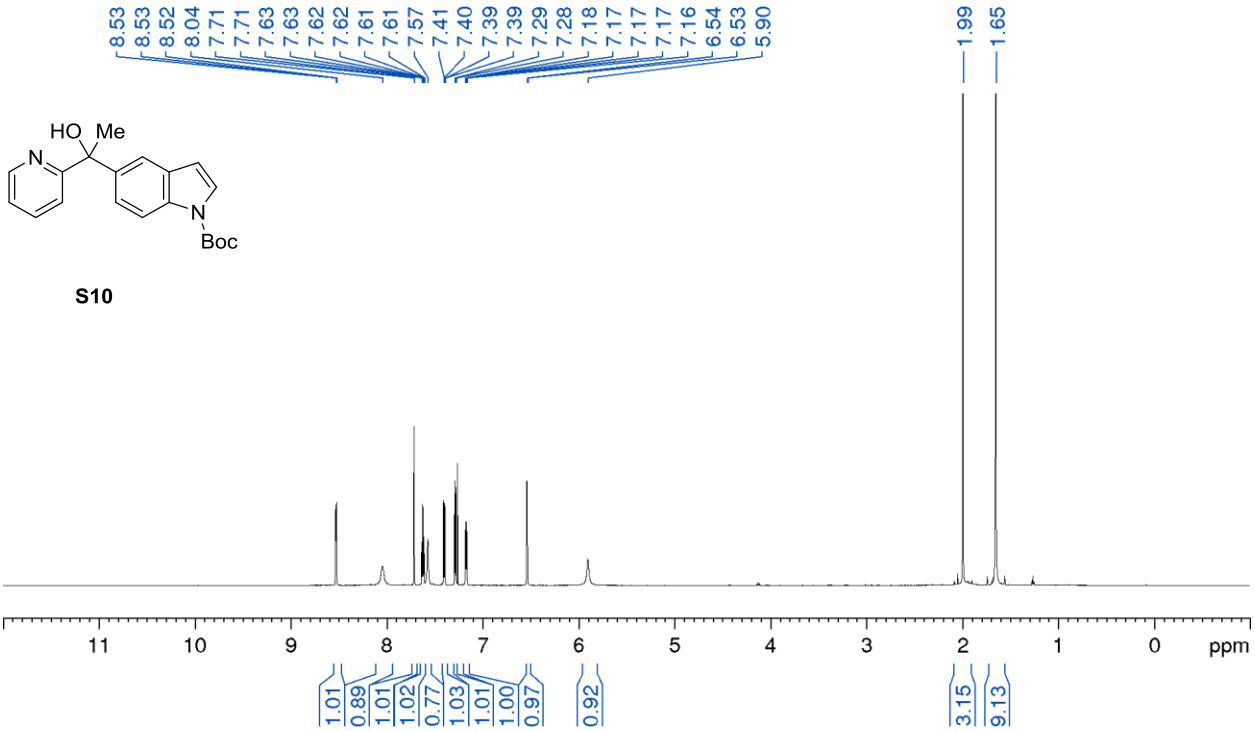
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S9**



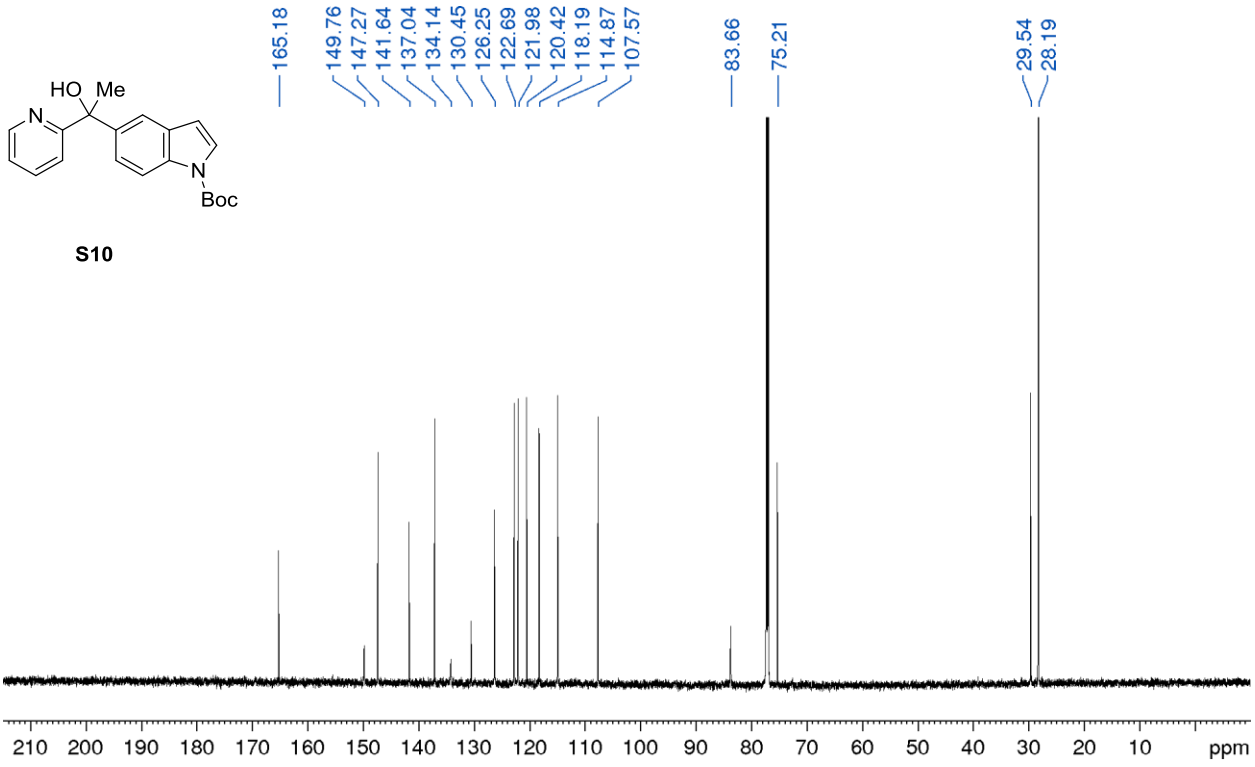

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S9**



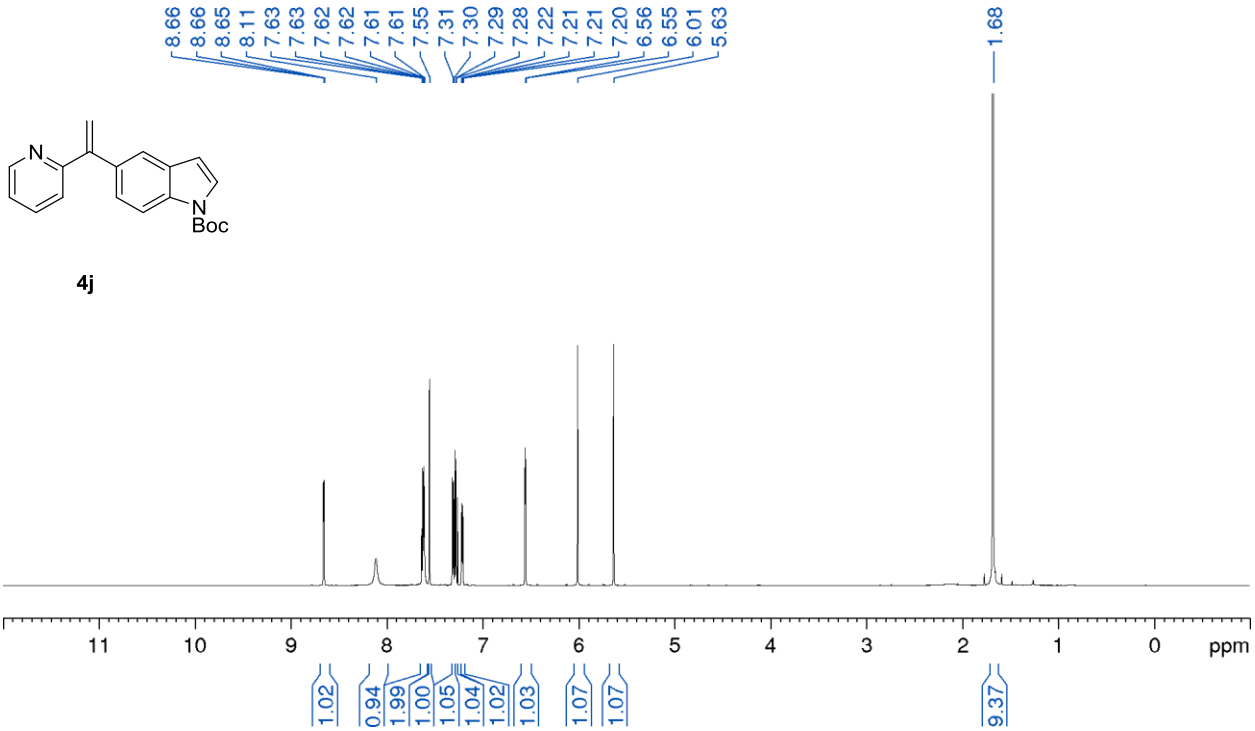
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **S10**



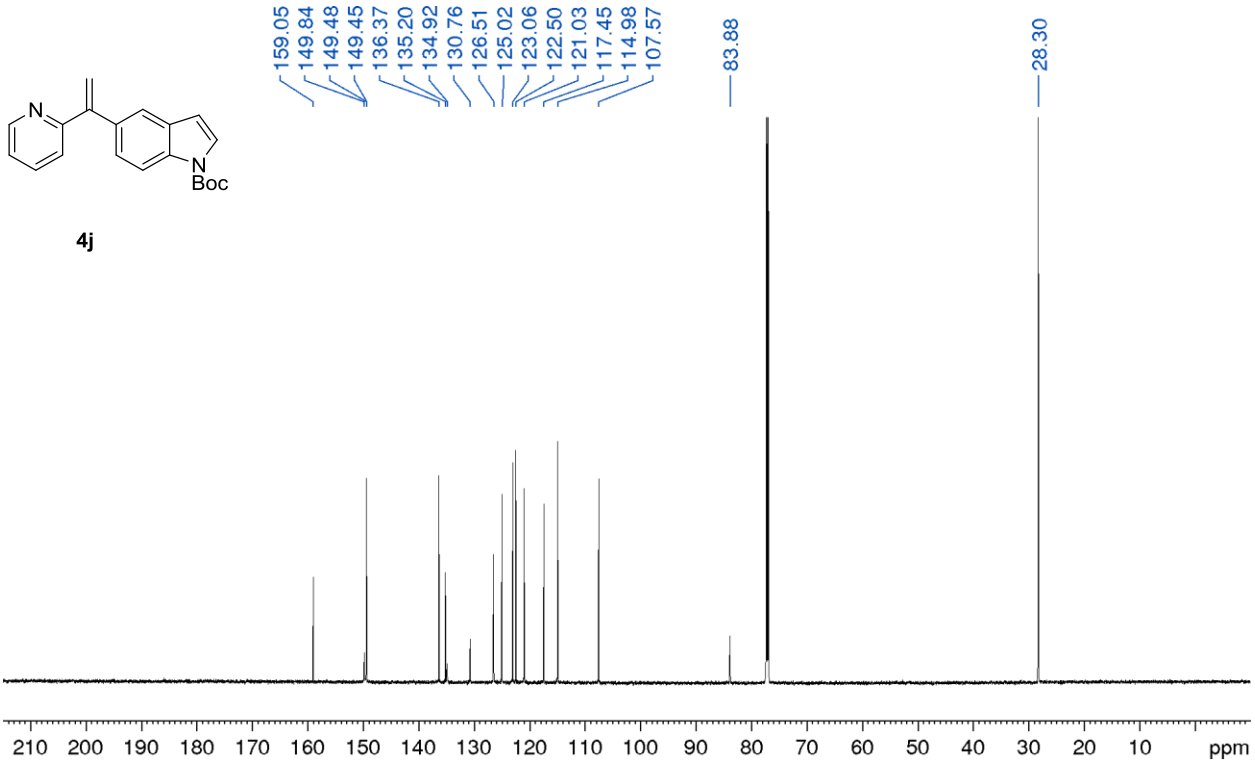

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **S10**



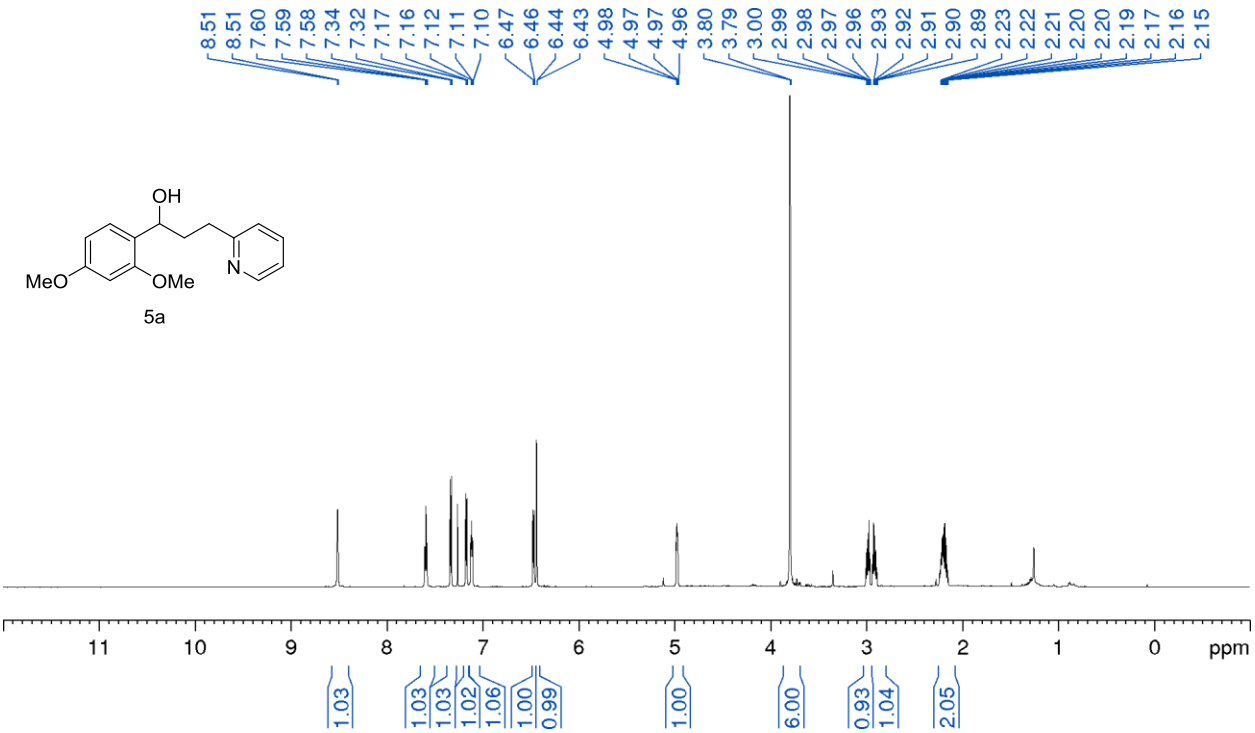
$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **4j**



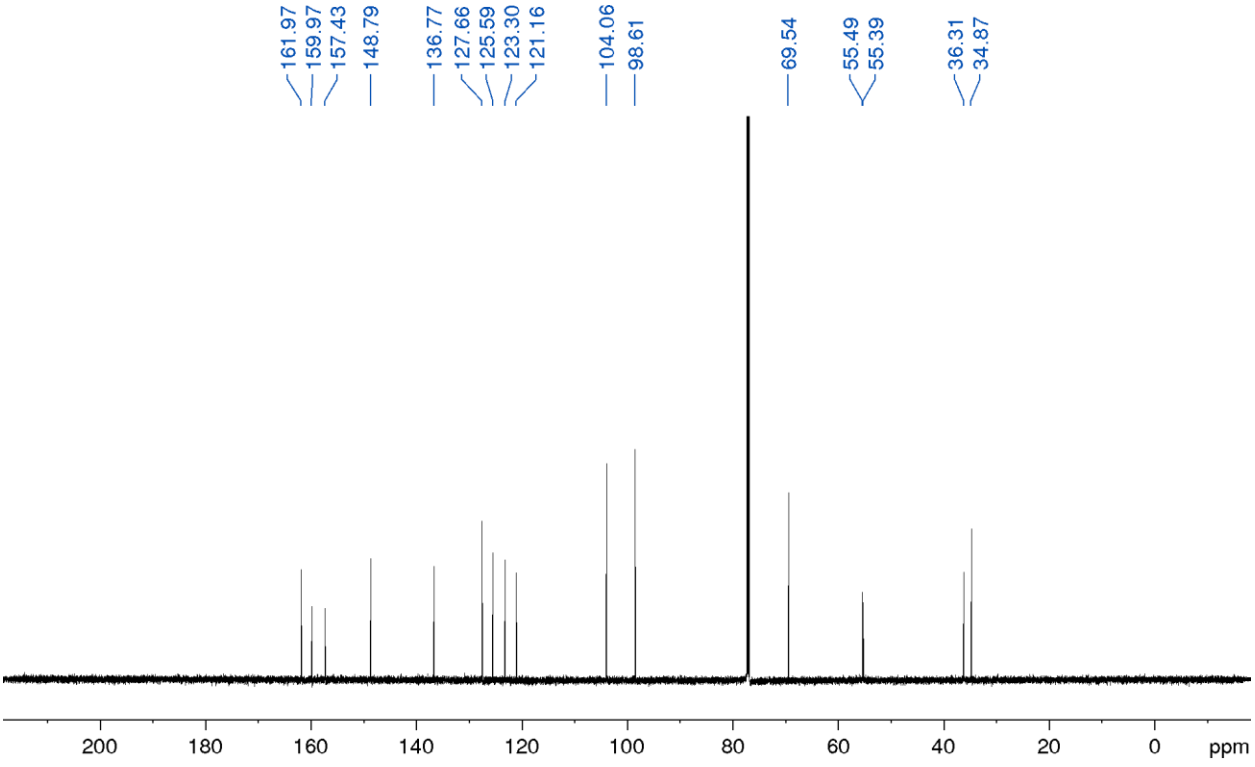

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **4j**



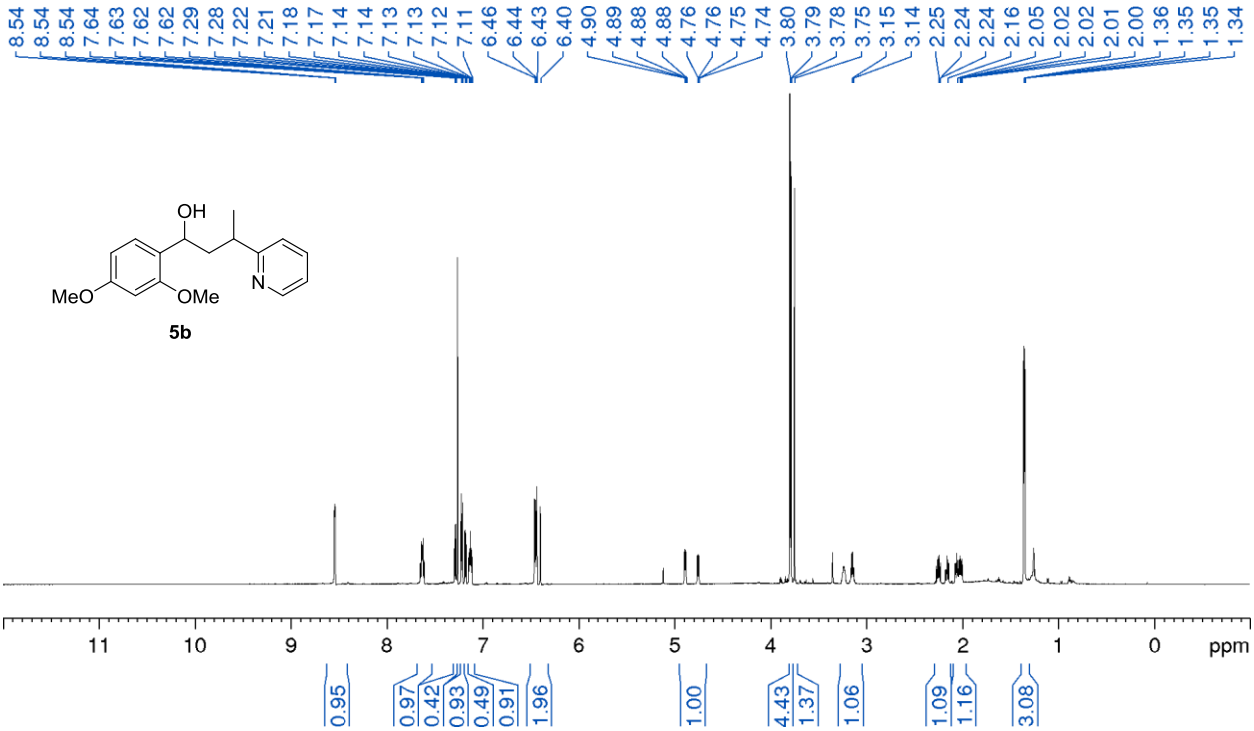
$^{1}$H NMR (700 MHz, $CDCl_3$) of **5a**



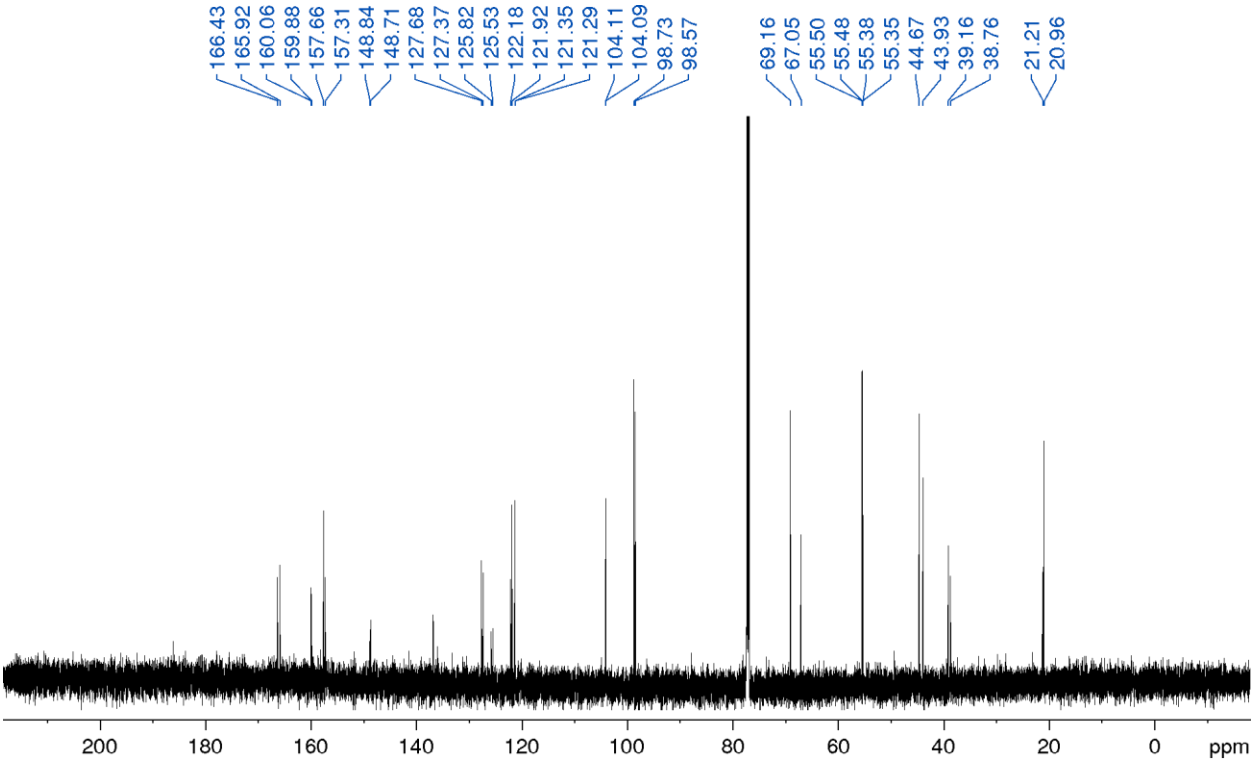

$^{13}$C NMR (176 MHz, $CDCl_3$) of **5a**



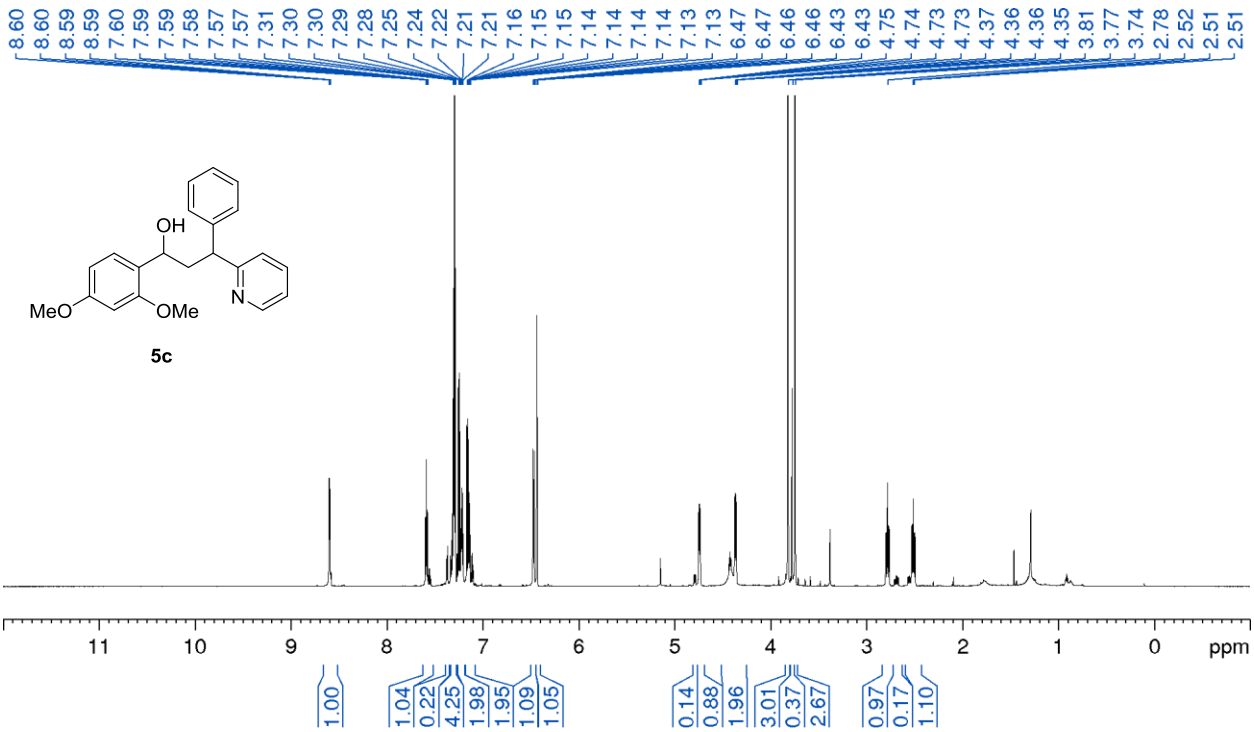
$^{1}$H NMR (700 MHz, $CDCl_3$) of **5b**



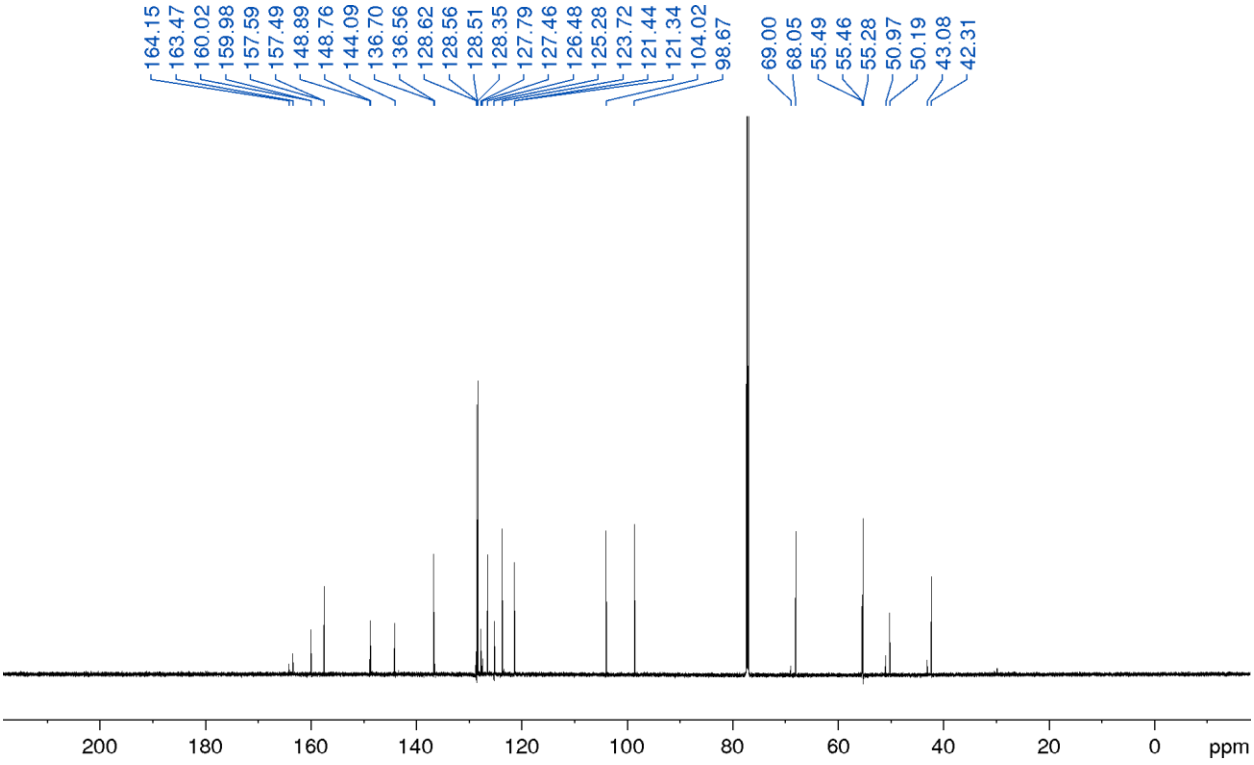

$^{13}$C NMR (176 MHz, $CDCl_3$) of **5b**



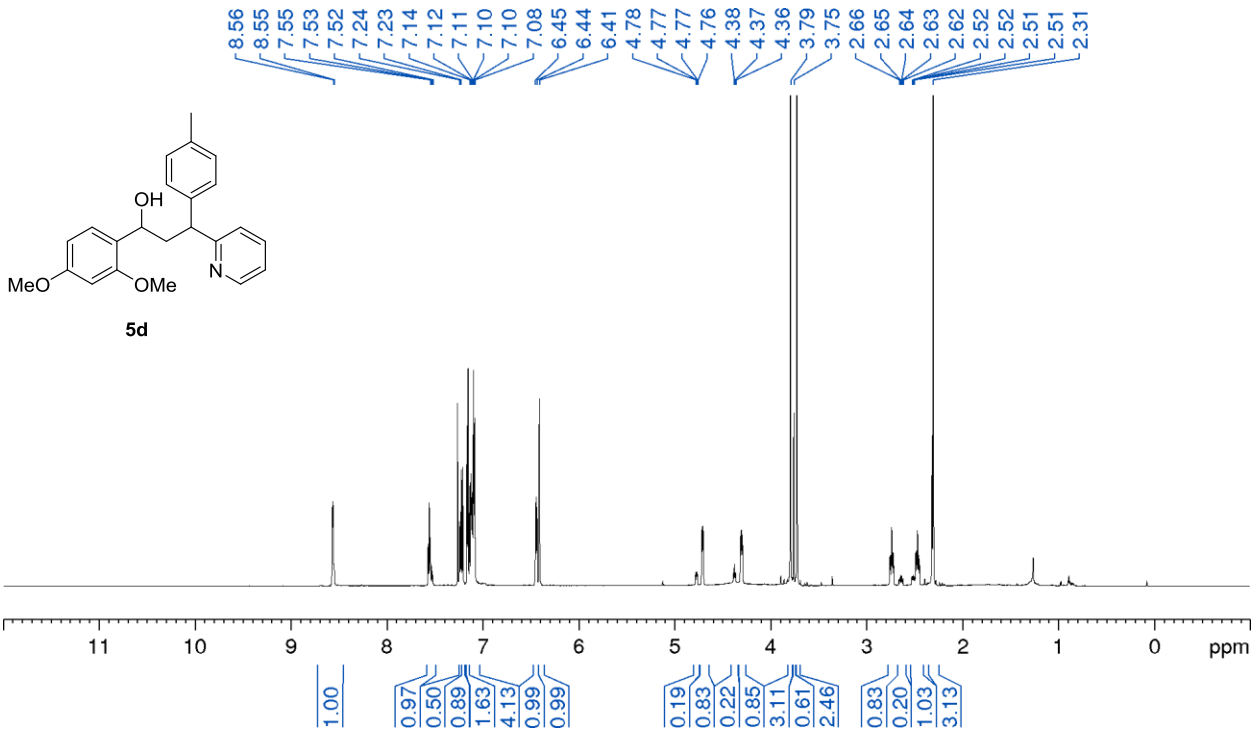
$^{1}$H NMR (700 MHz, $CDCl_3$) of **5c**



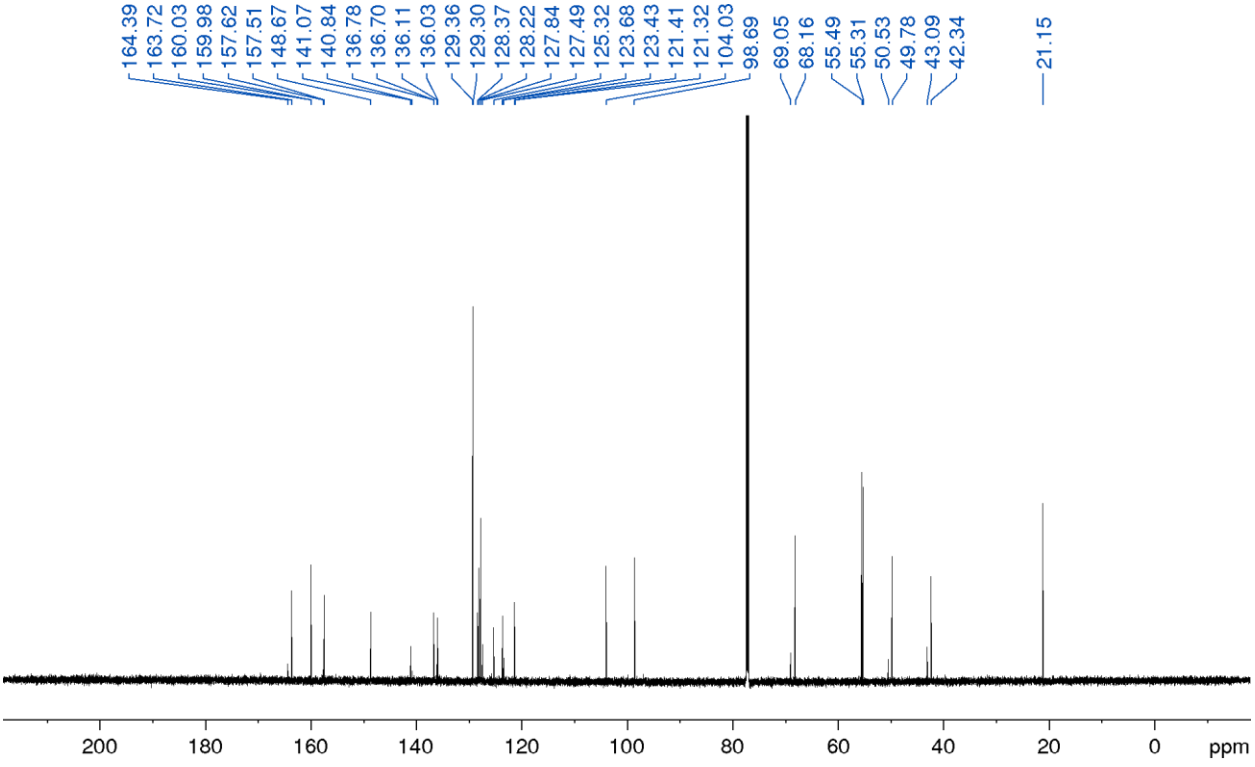

$^{13}$C NMR (176 MHz, $CDCl_3$) of **5c**



$^{1}$H NMR (700 MHz, $CDCl_3$) of **5d**

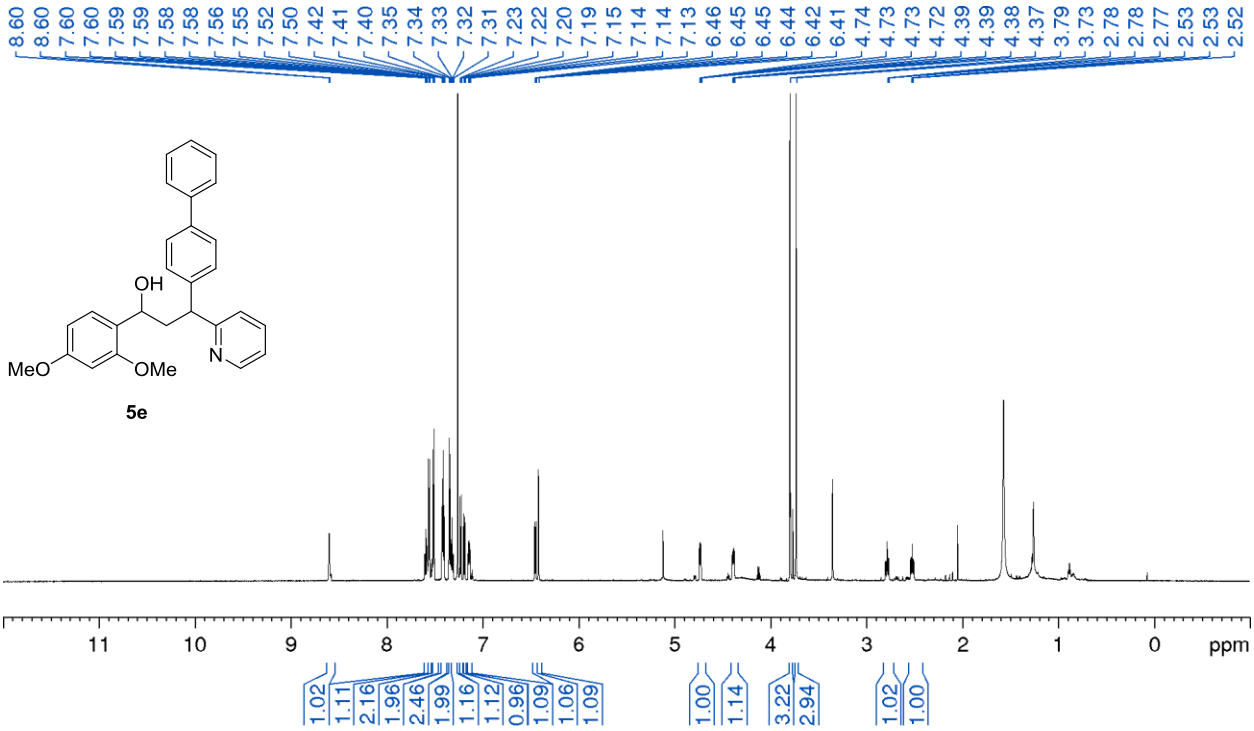



$^{13}$C NMR (176 MHz, $CDCl_3$) of **5d**

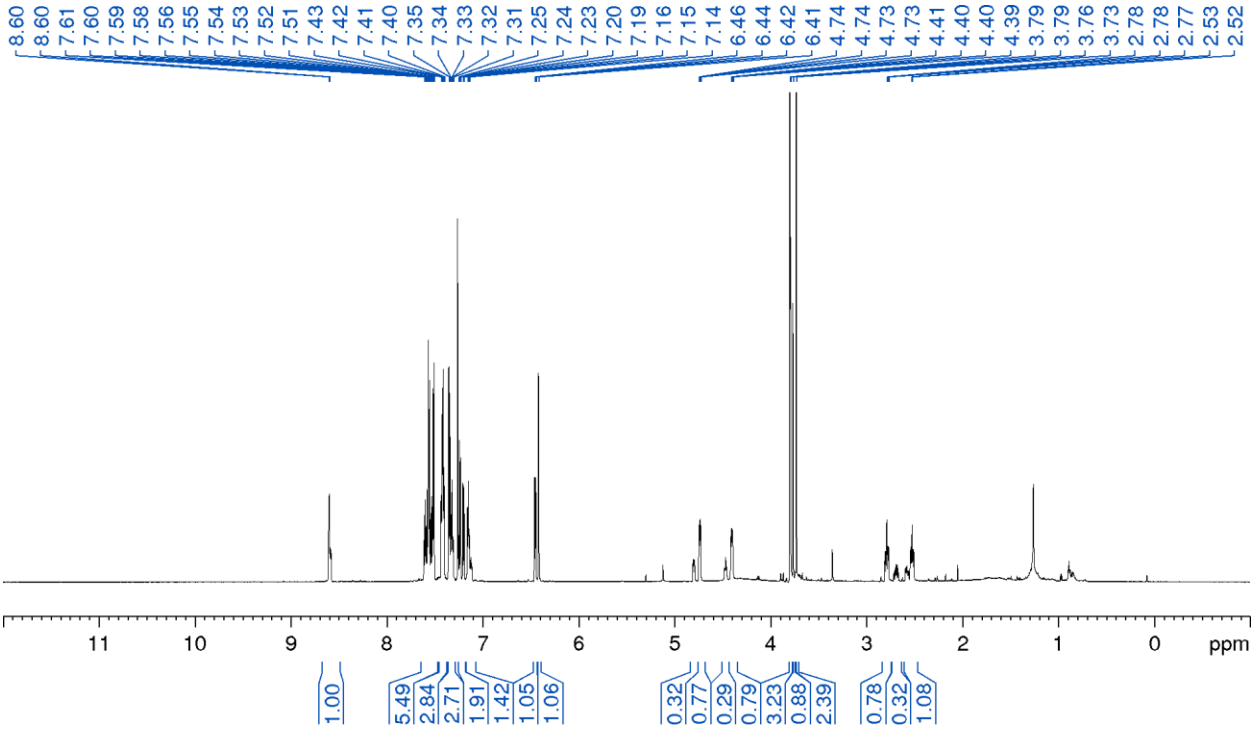


$^1$H NMR (700 MHz, $CDCl_3$) of **5e**

Diastereomer 1

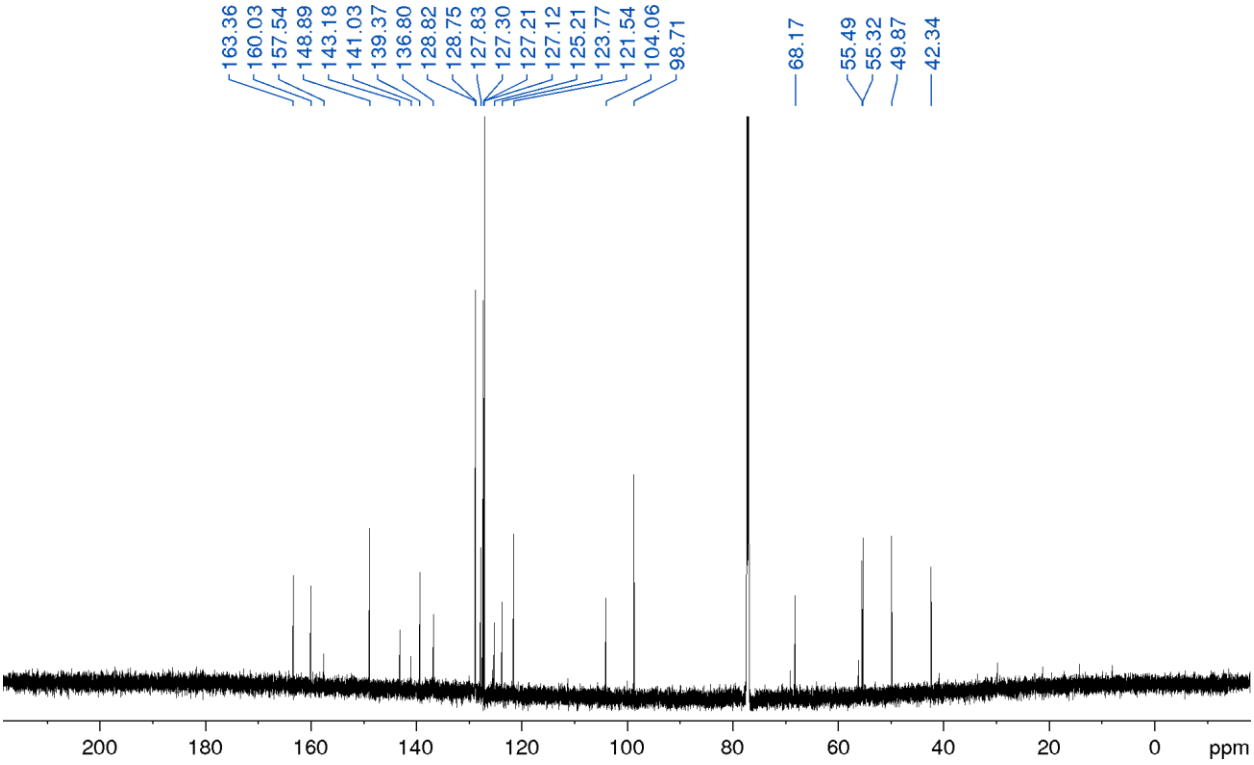



A mixture of two diastereomers

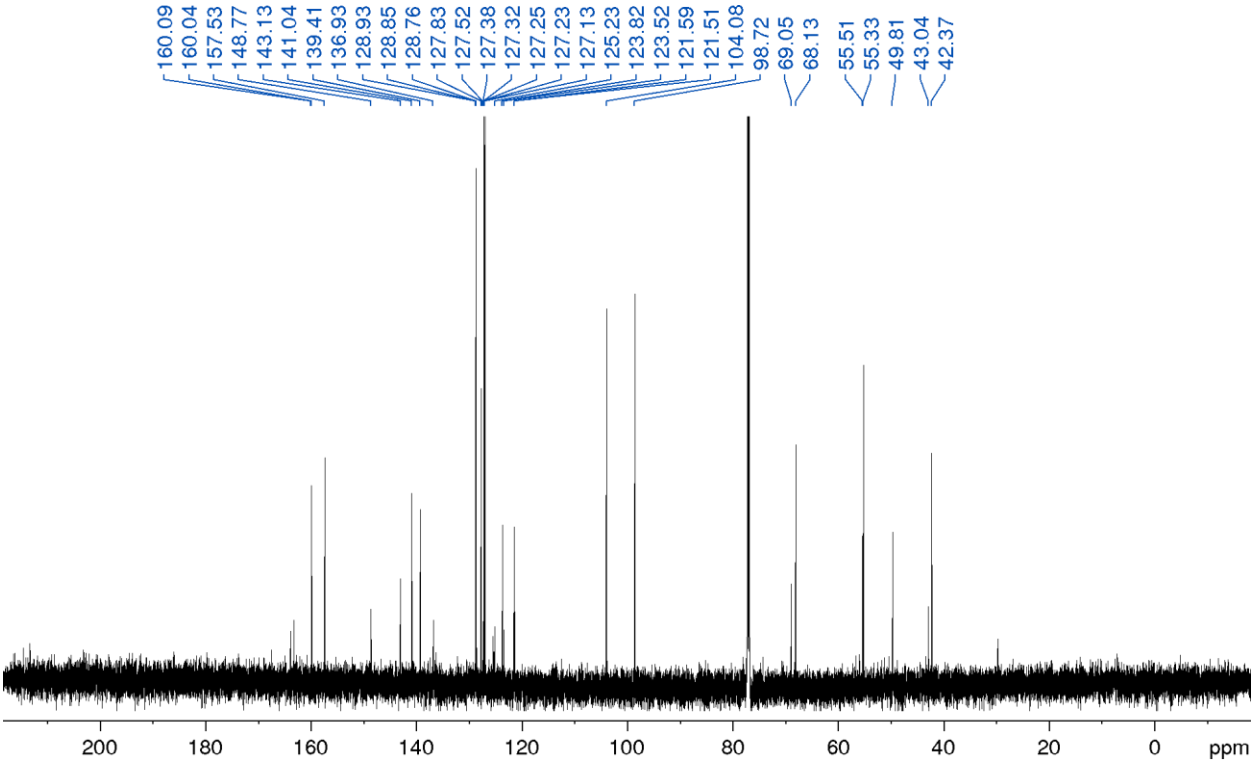


$^{13}C$ NMR (176 MHz, $CDCl_3$) of **5e**

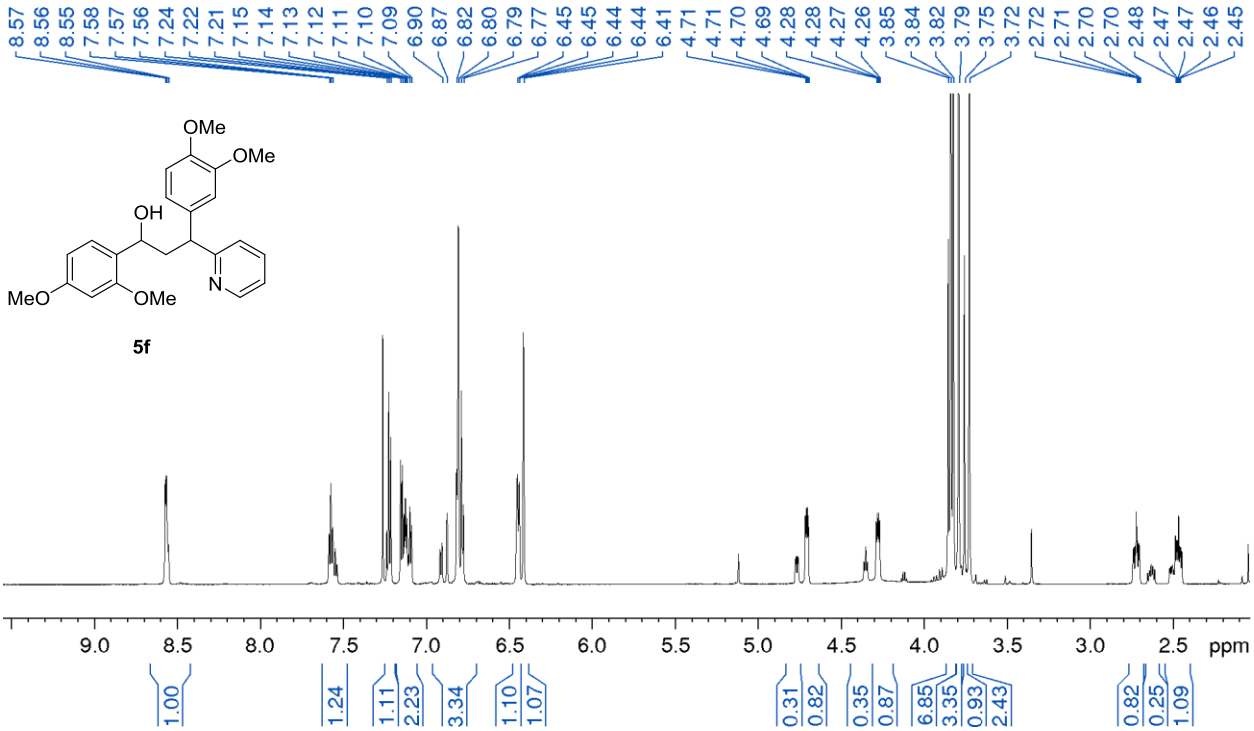
Diastereomer 1



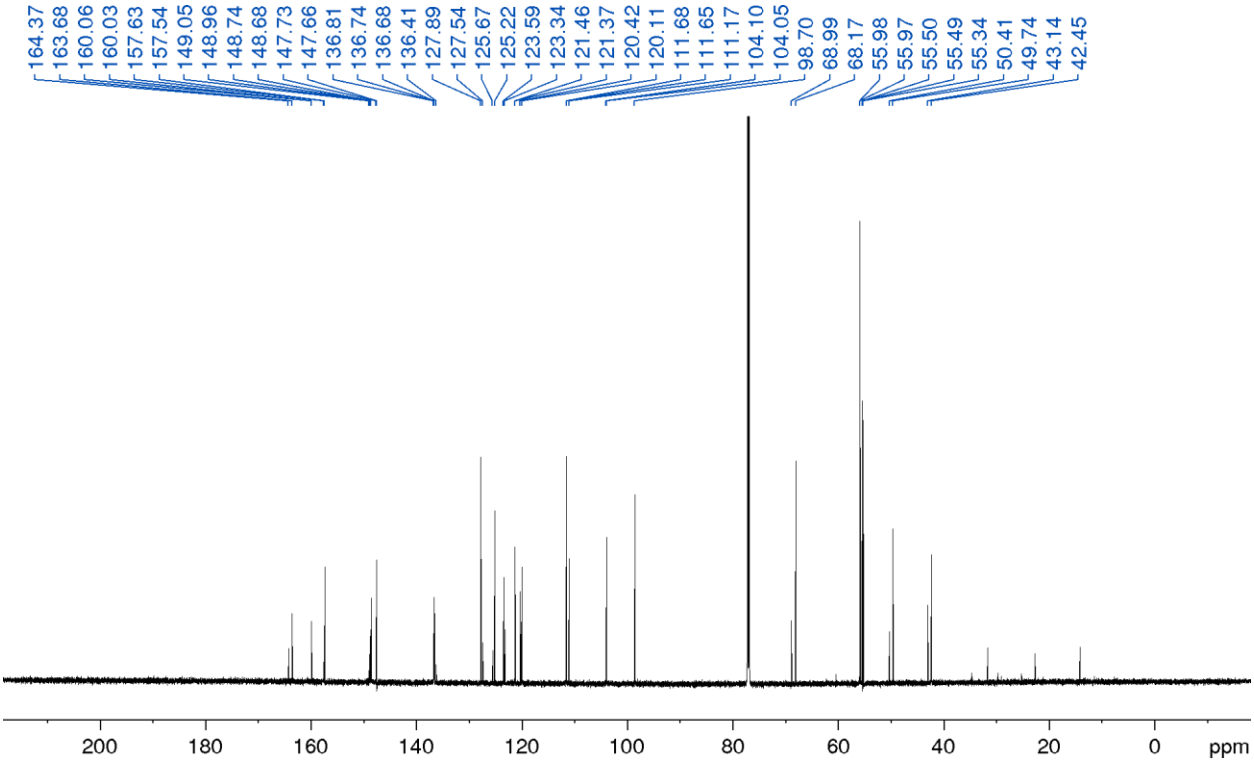

A mix of two diastereomers



$^{1}$H NMR (700 MHz, $CDCl_3$) of **5f**

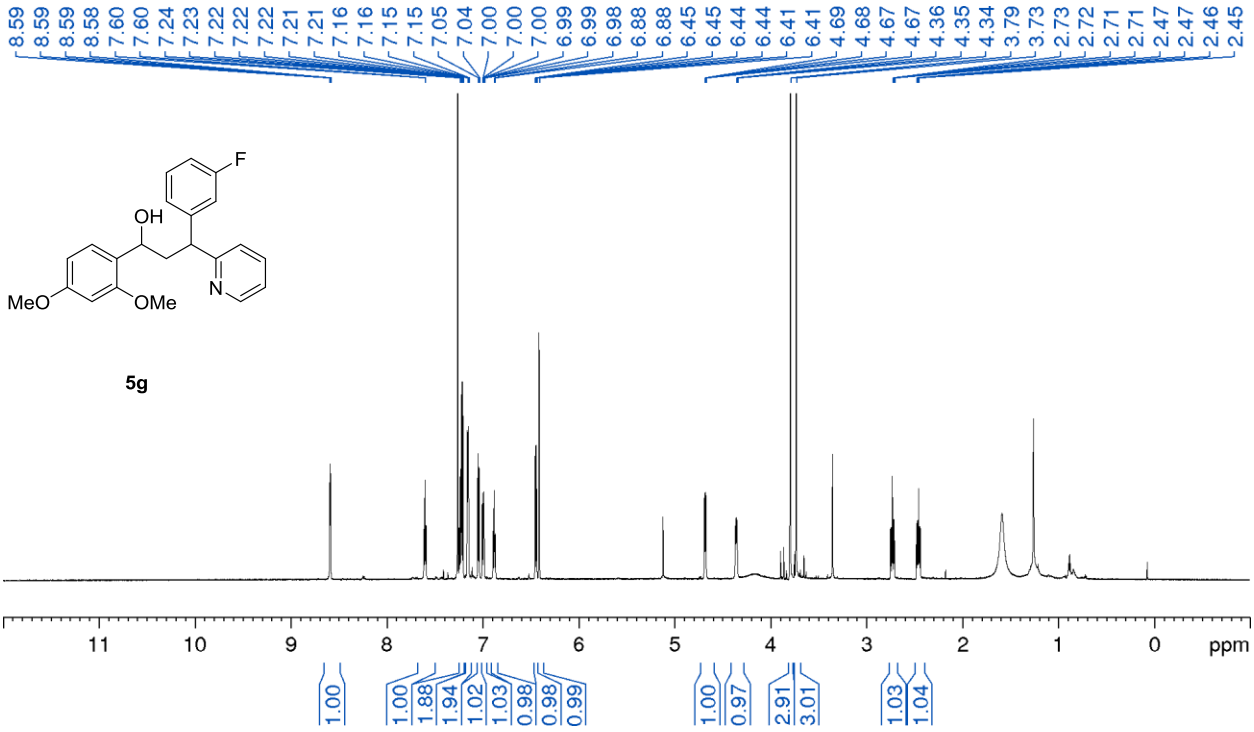



$^{13}$C NMR (176 MHz, $CDCl_3$) of **5f**

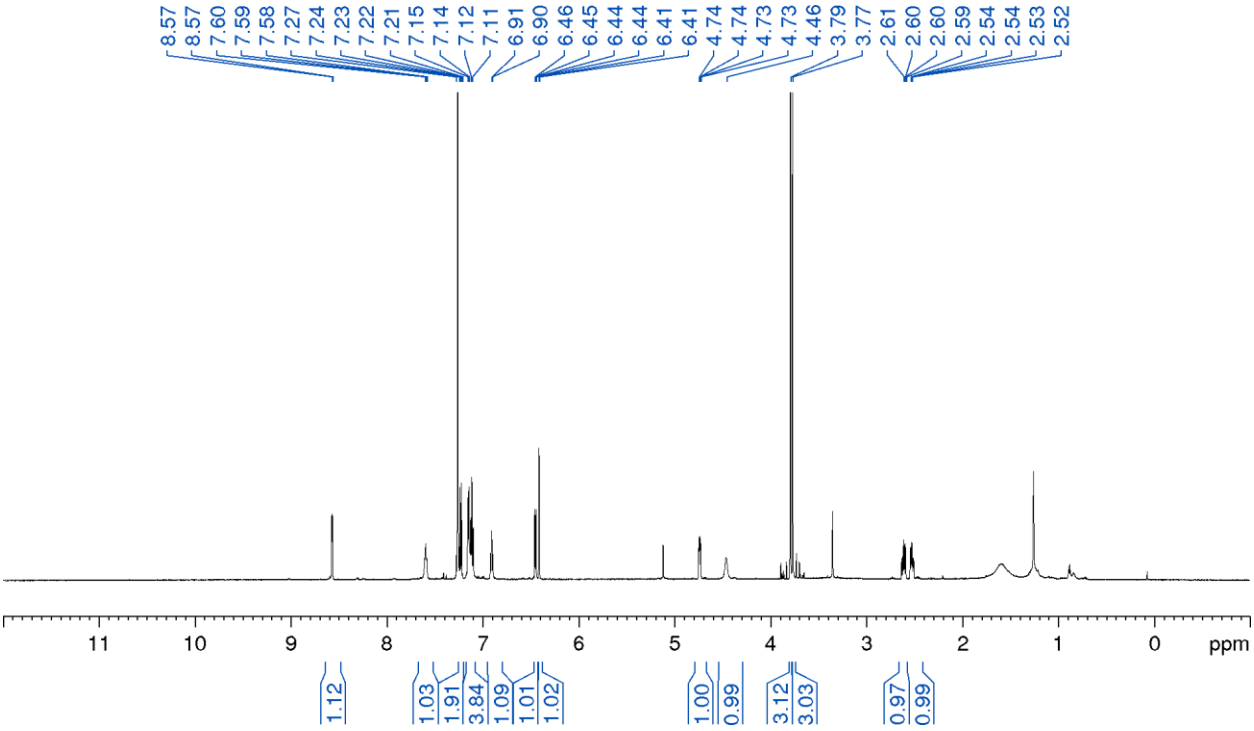


$^1$H NMR (700 MHz, $CDCl_3$) of **5g**

Diastereome 1

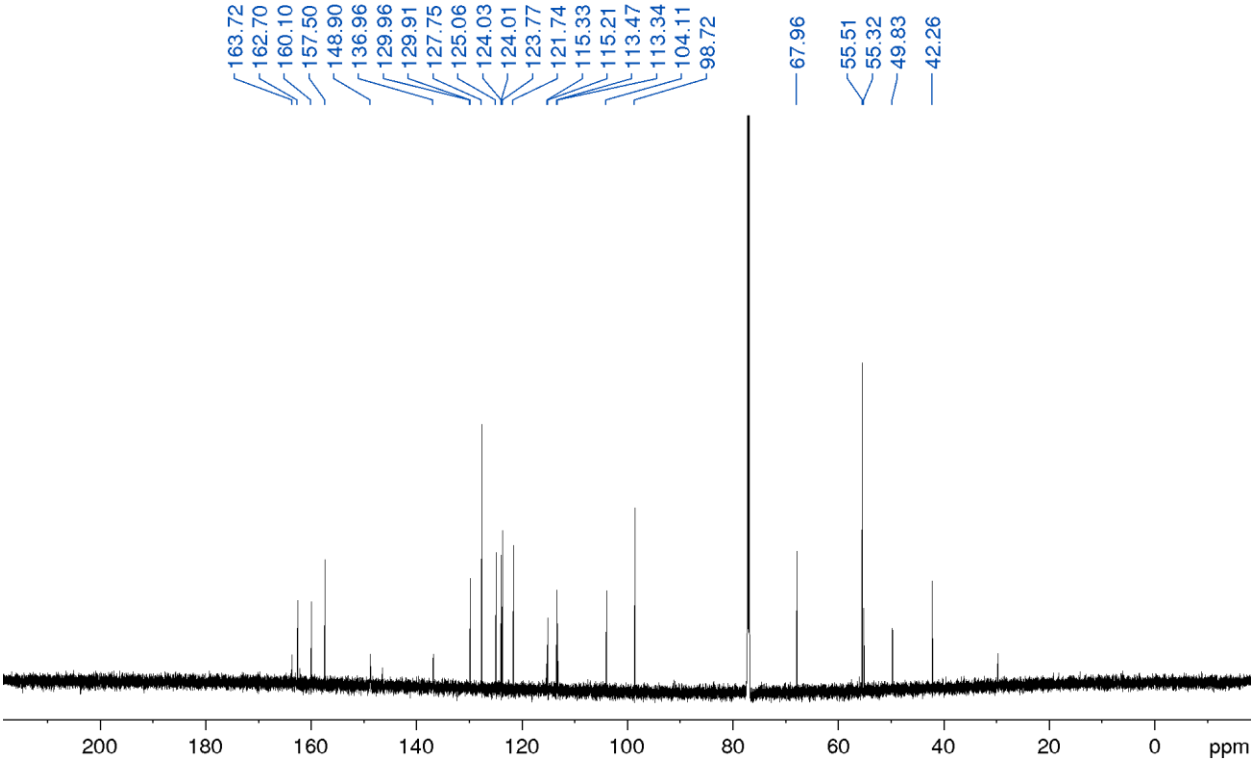



Diastereomer 2

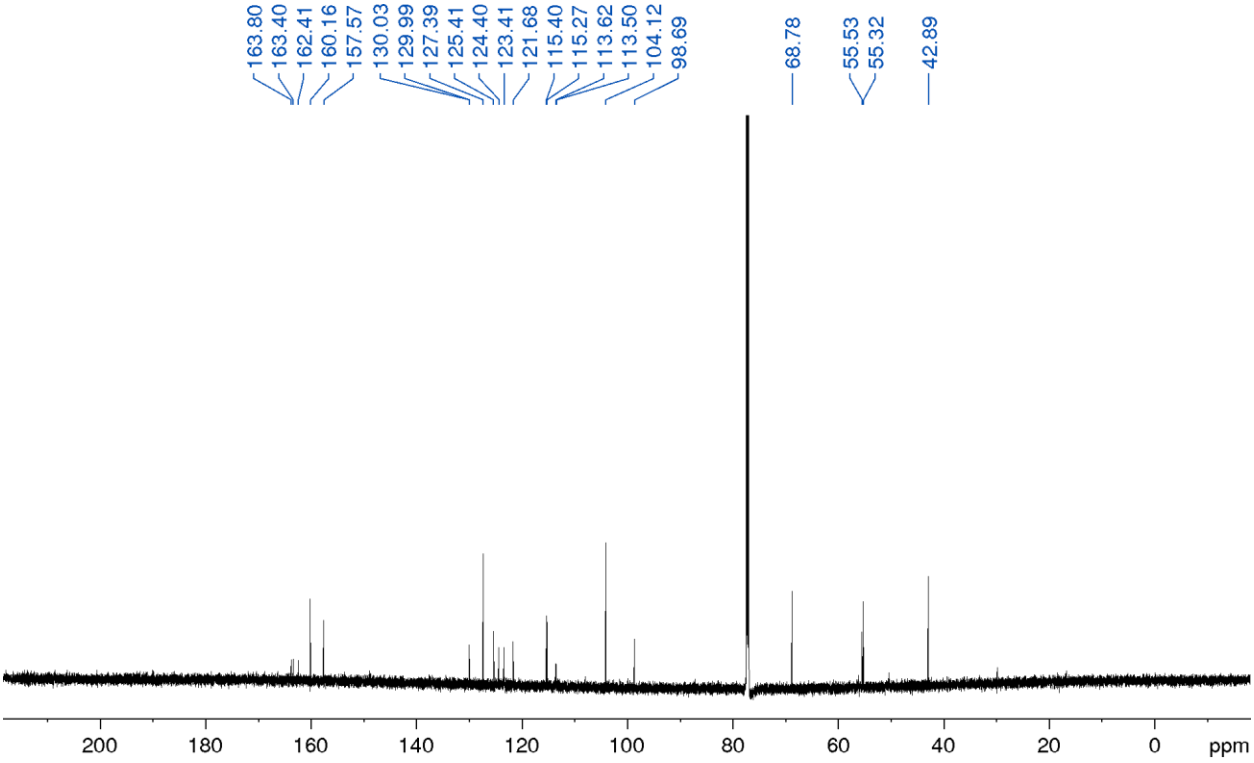


$^{13}C$ NMR (176 MHz, $CDCl_3$) of **5g**

Diastereomer 1

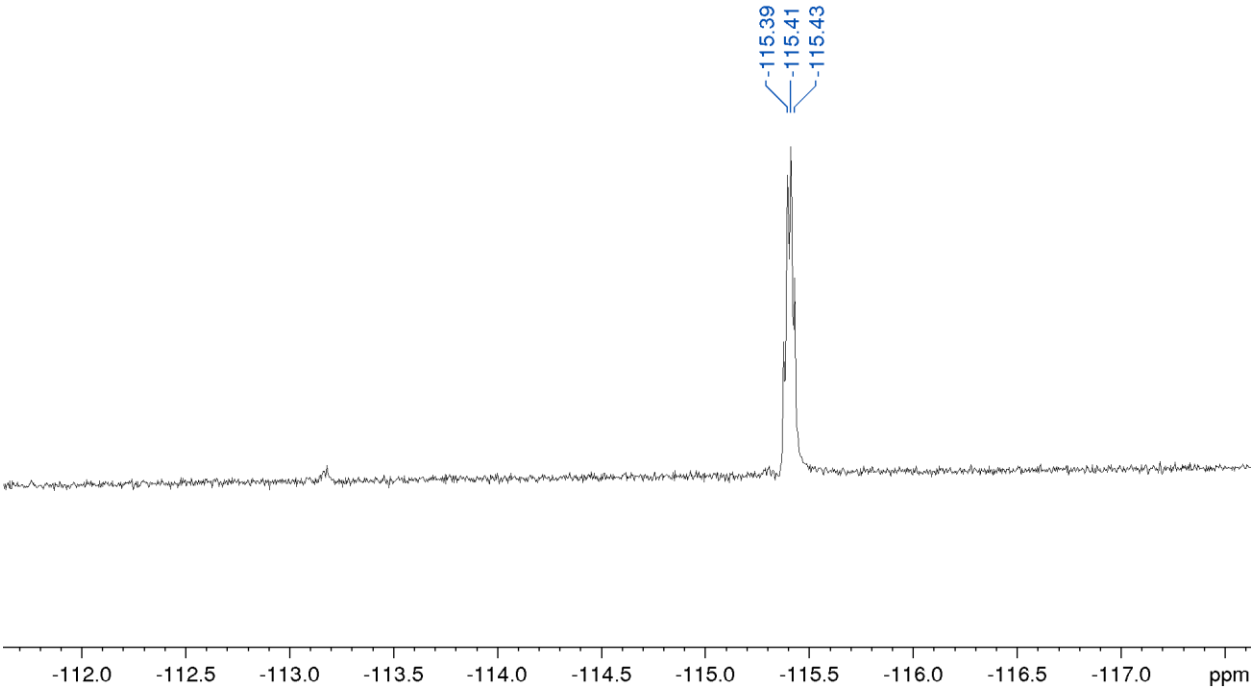



Diastereomer 2

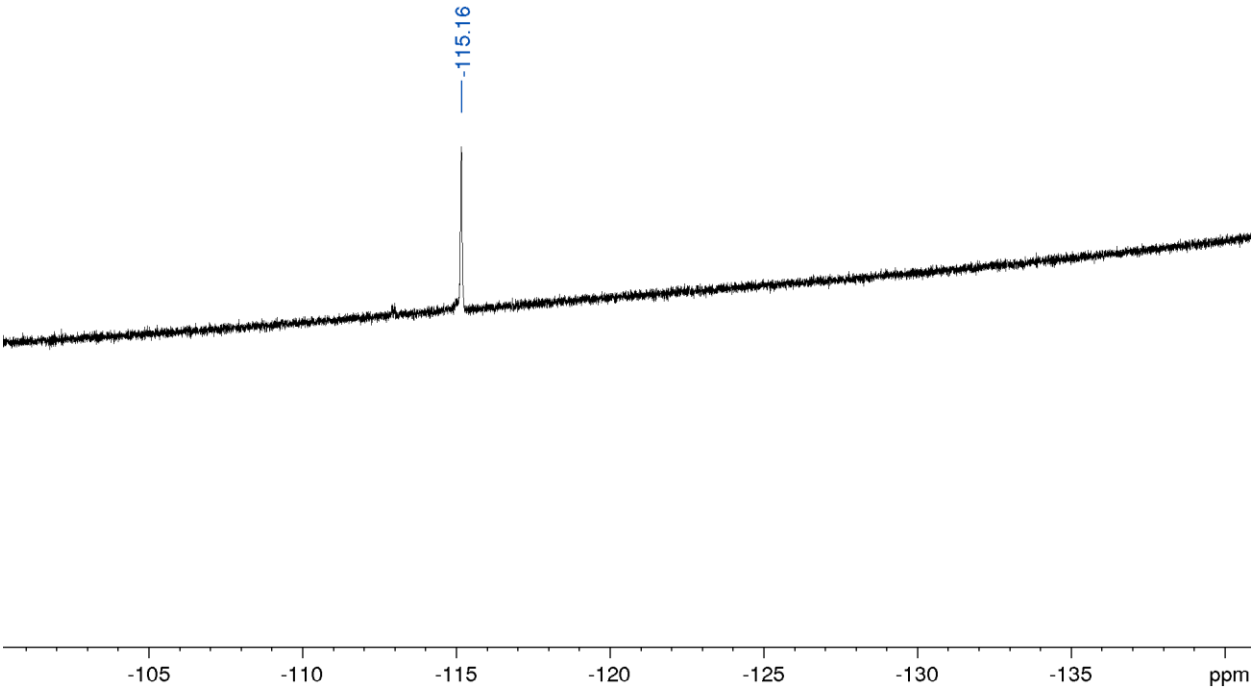


$^{19}F$ NMR (376 MHz, $CDCl_3$,) of **5g**

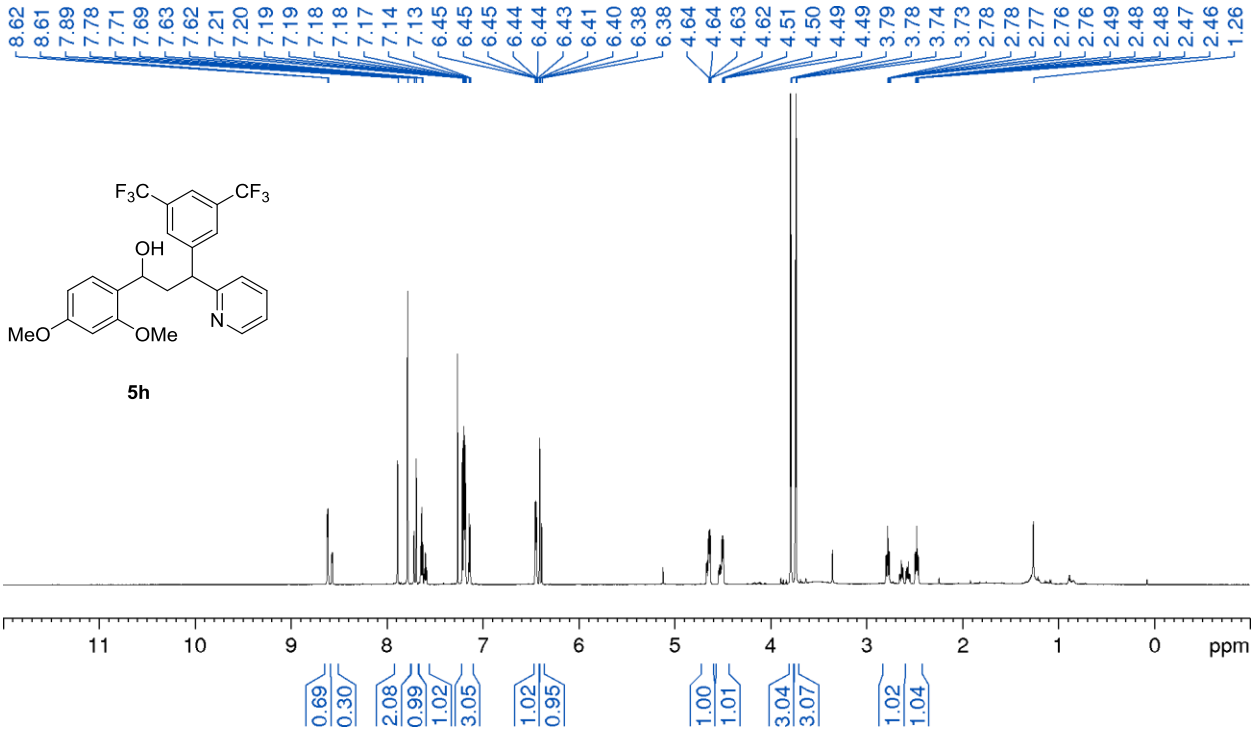
Diastereomer 1



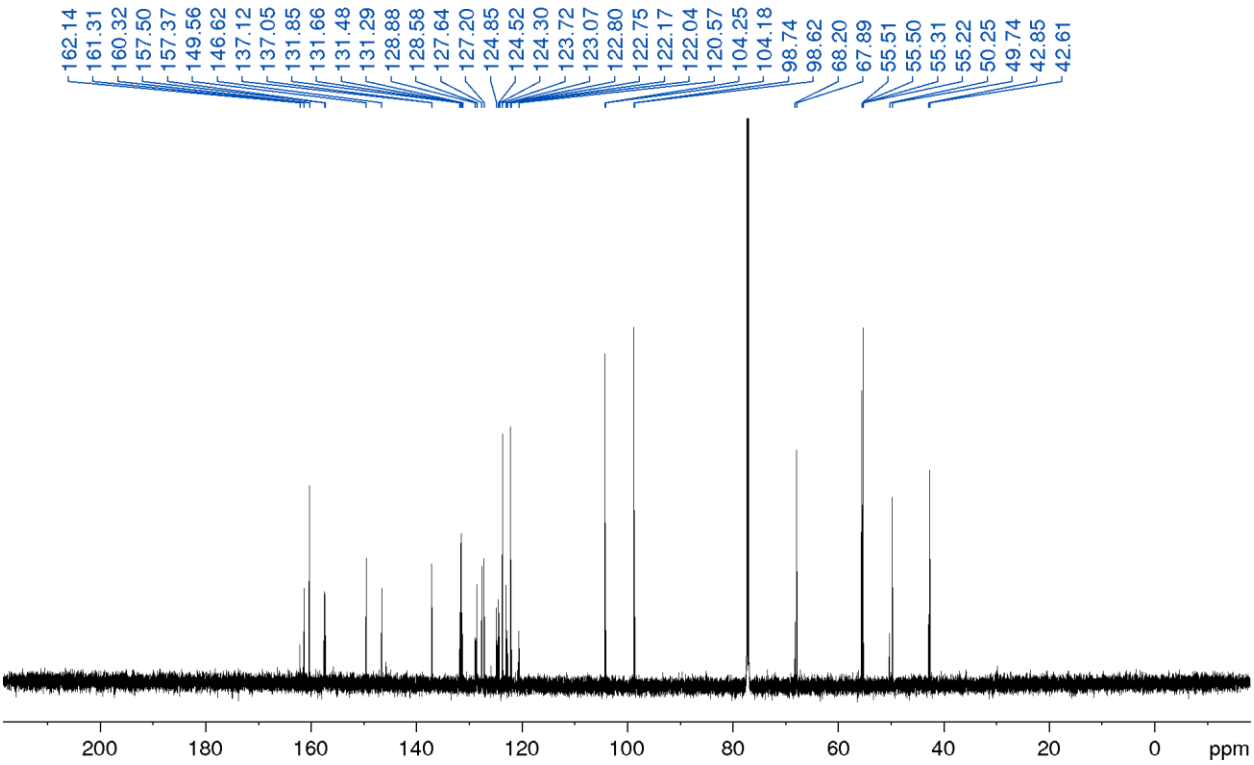

Diastereomer 2



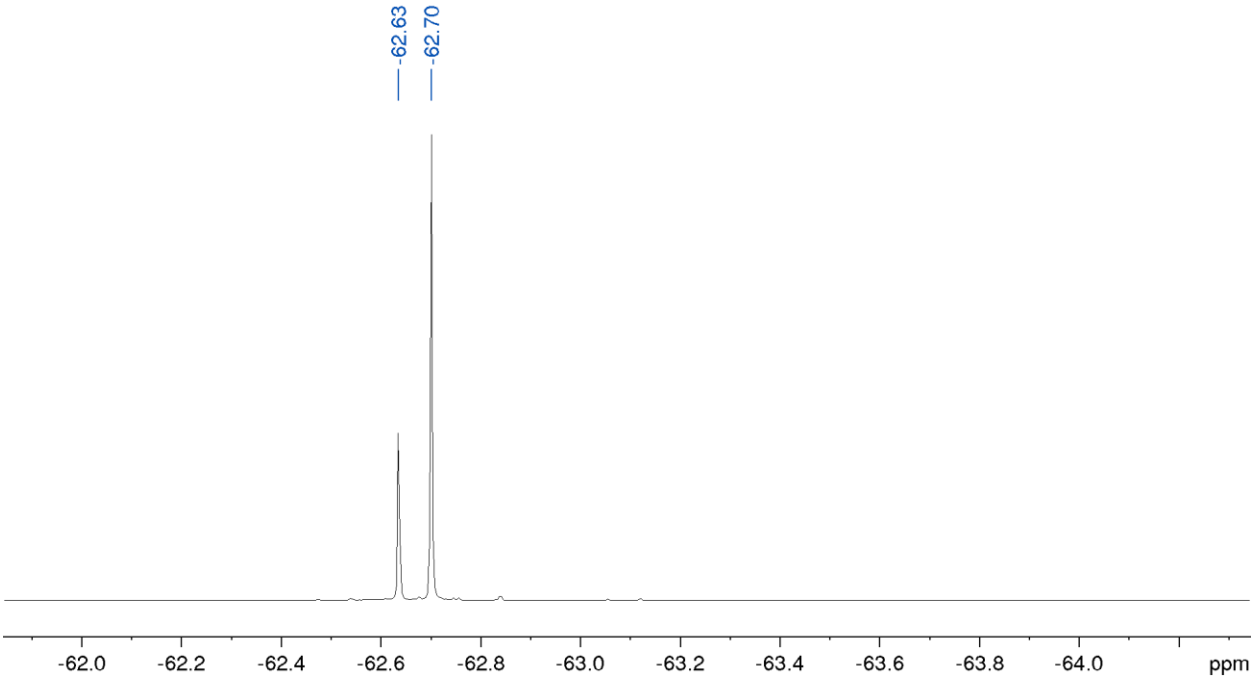
$^{1}$H NMR (700 MHz, $CDCl_3$) of **5h**



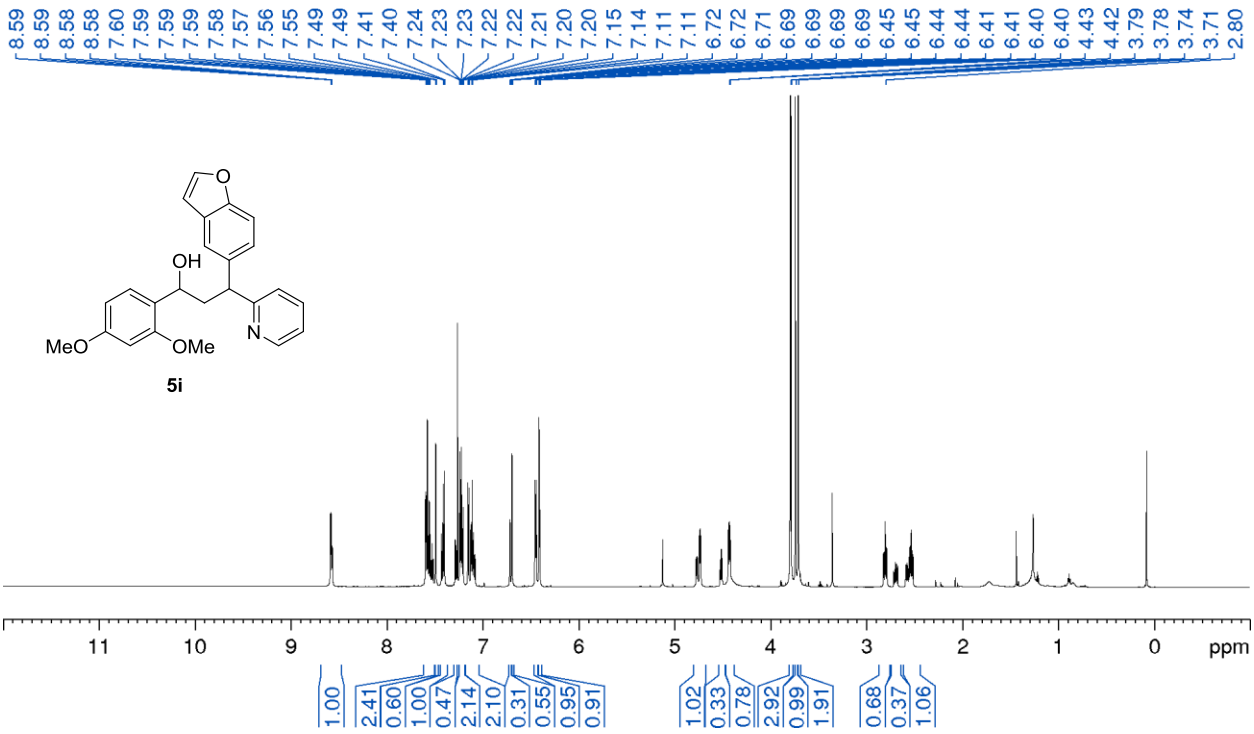

$^{13}$C NMR (176 MHz, $CDCl_3$) of **5h**



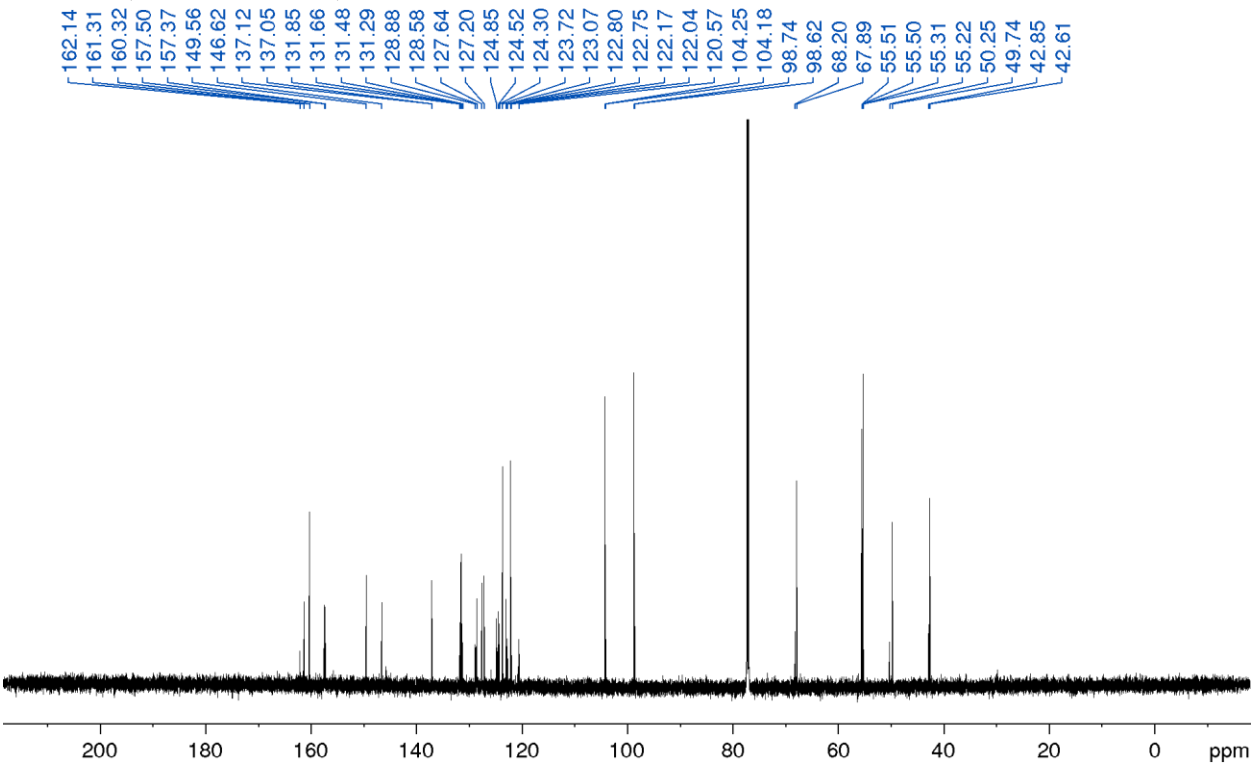
$^{19}$F NMR (376 MHz, $CDCl_3$,) of **5h**




$^{1}$H NMR (700 MHz, $CDCl_3$) of **5i**

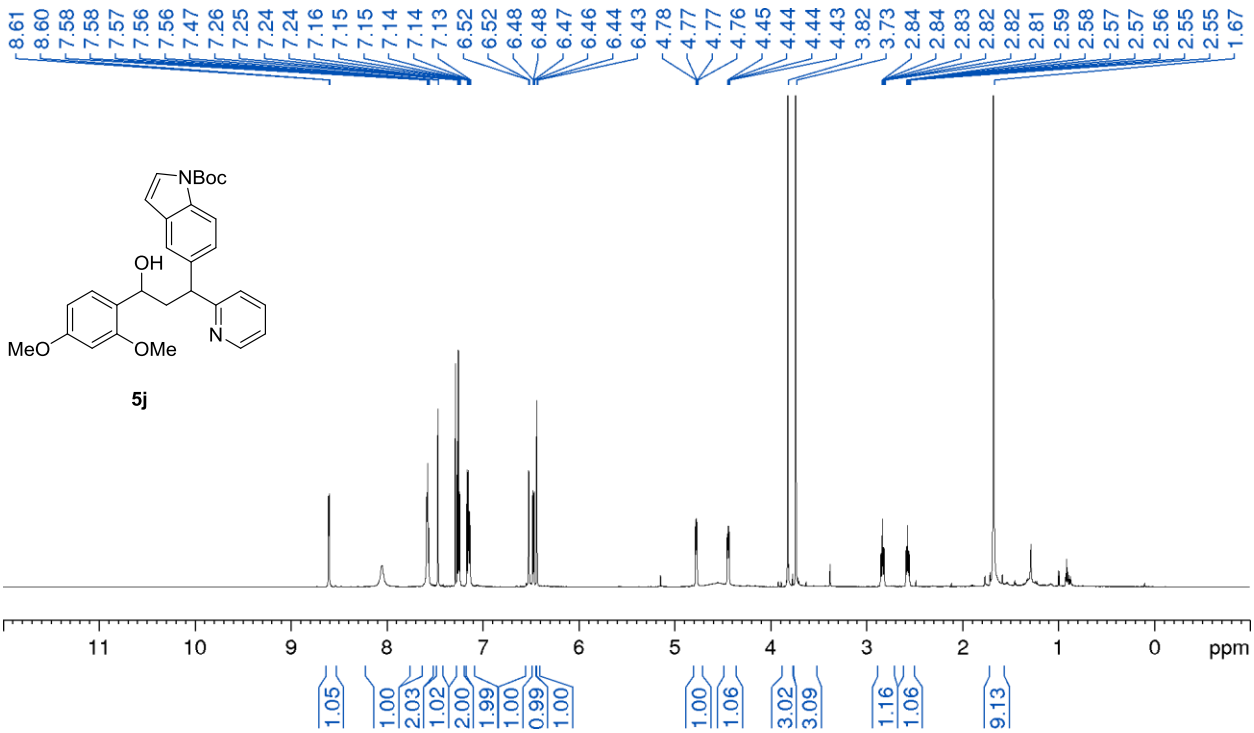


$^{13}$C NMR (176 MHz, $CDCl_3$) of **5i**

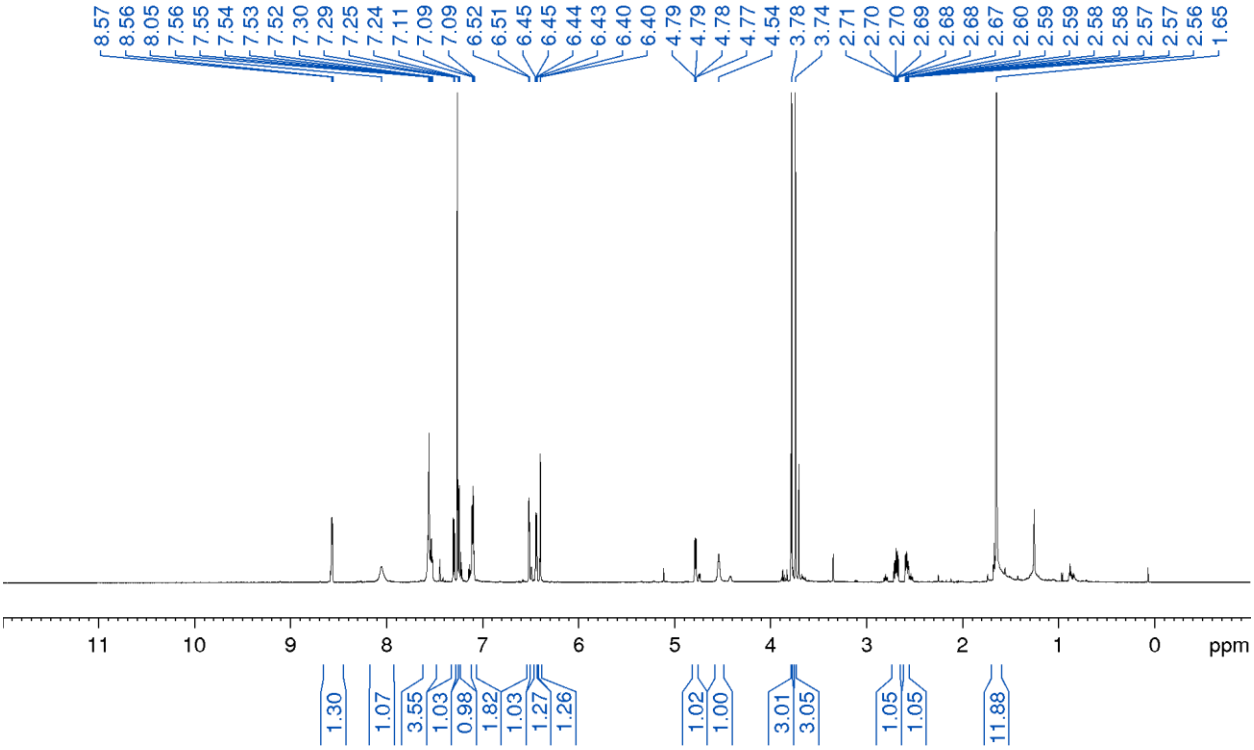



$^{1}$H NMR (700 MHz, $CDCl_3$) of **5j**

Diastereomer 1

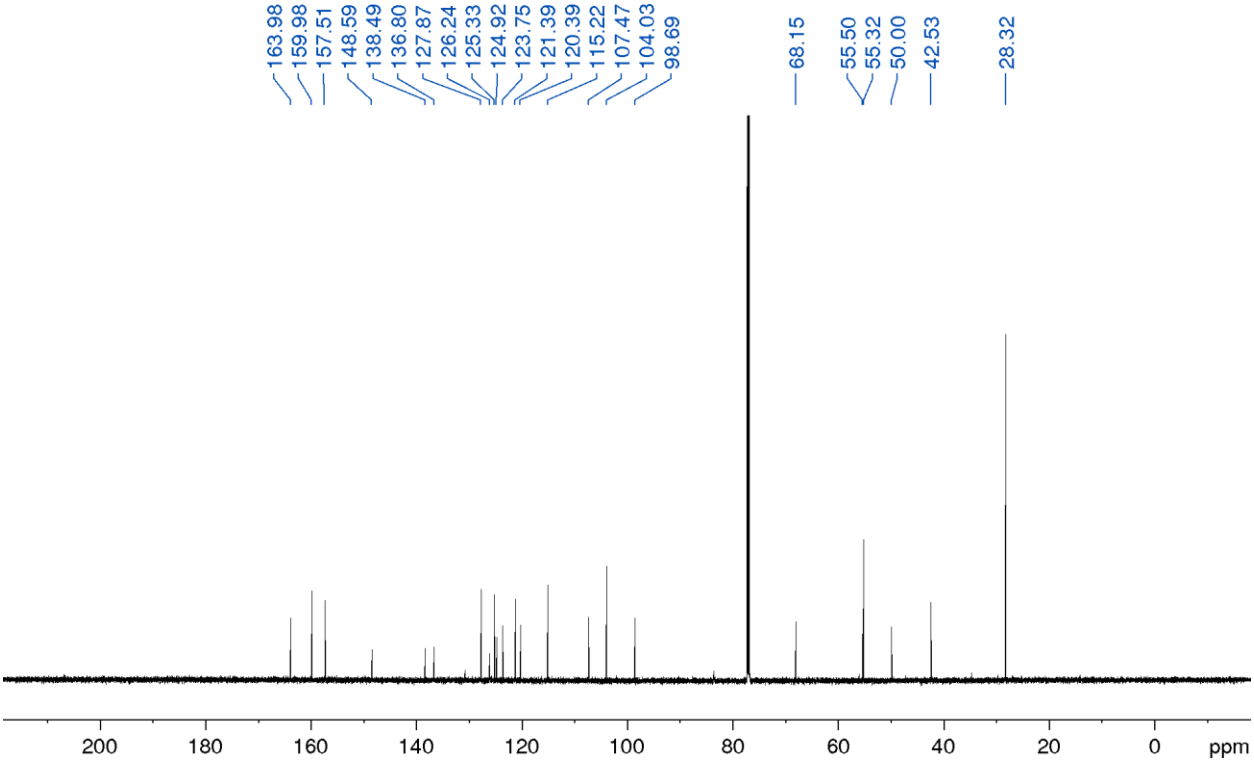


Diastereomer 2

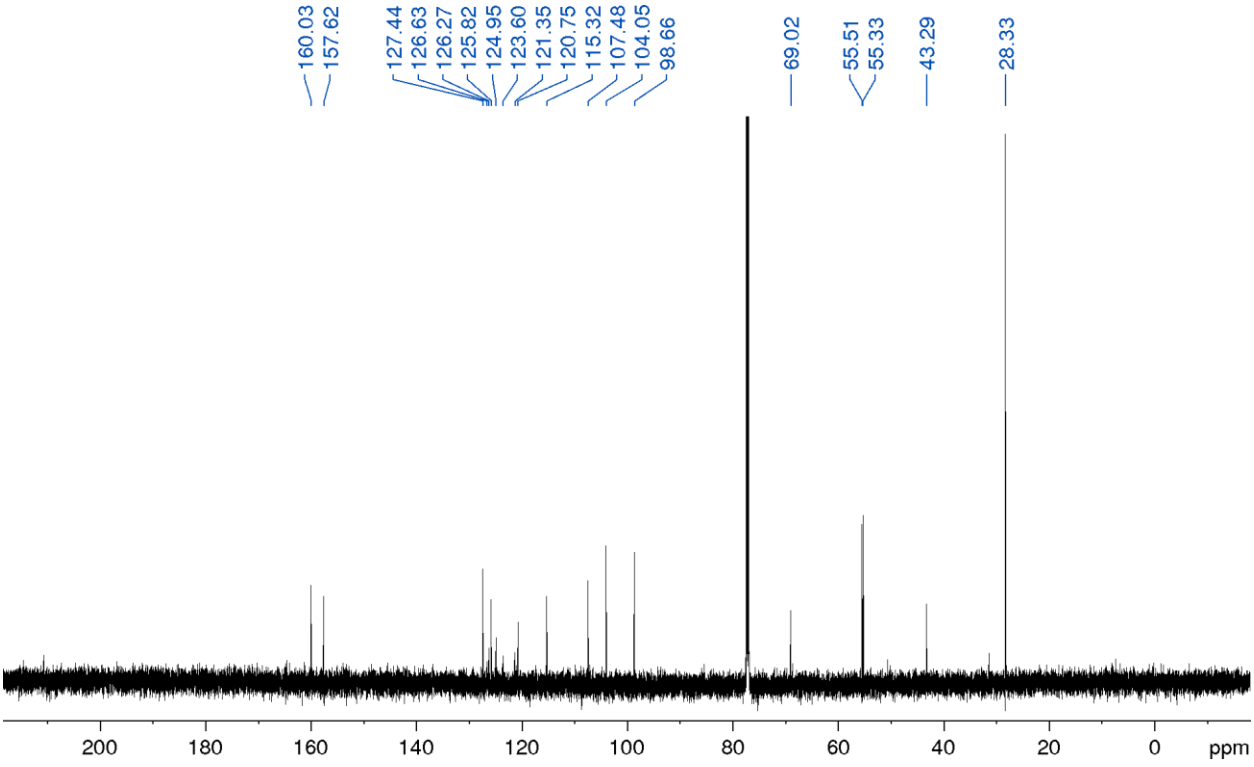



$^{13}C$ NMR (176 MHz, $CDCl_3$) of **5j**

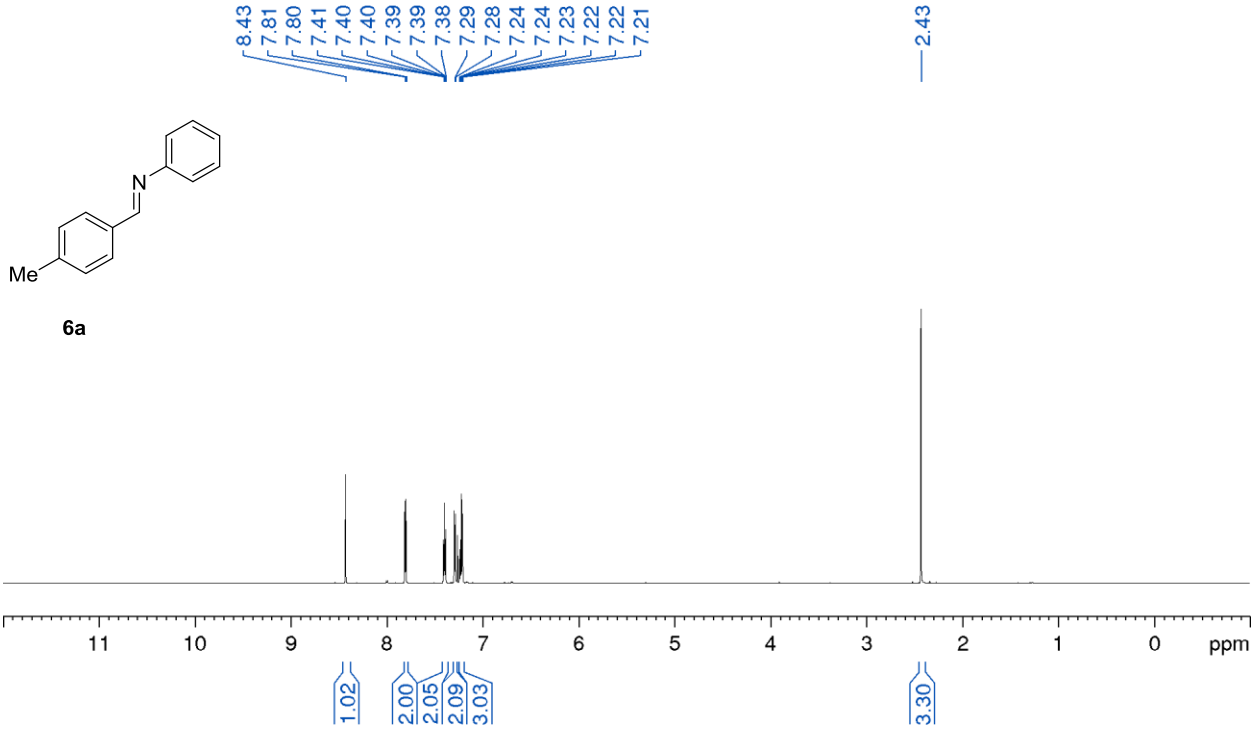
Diastereomer 1



Diastereomer 2

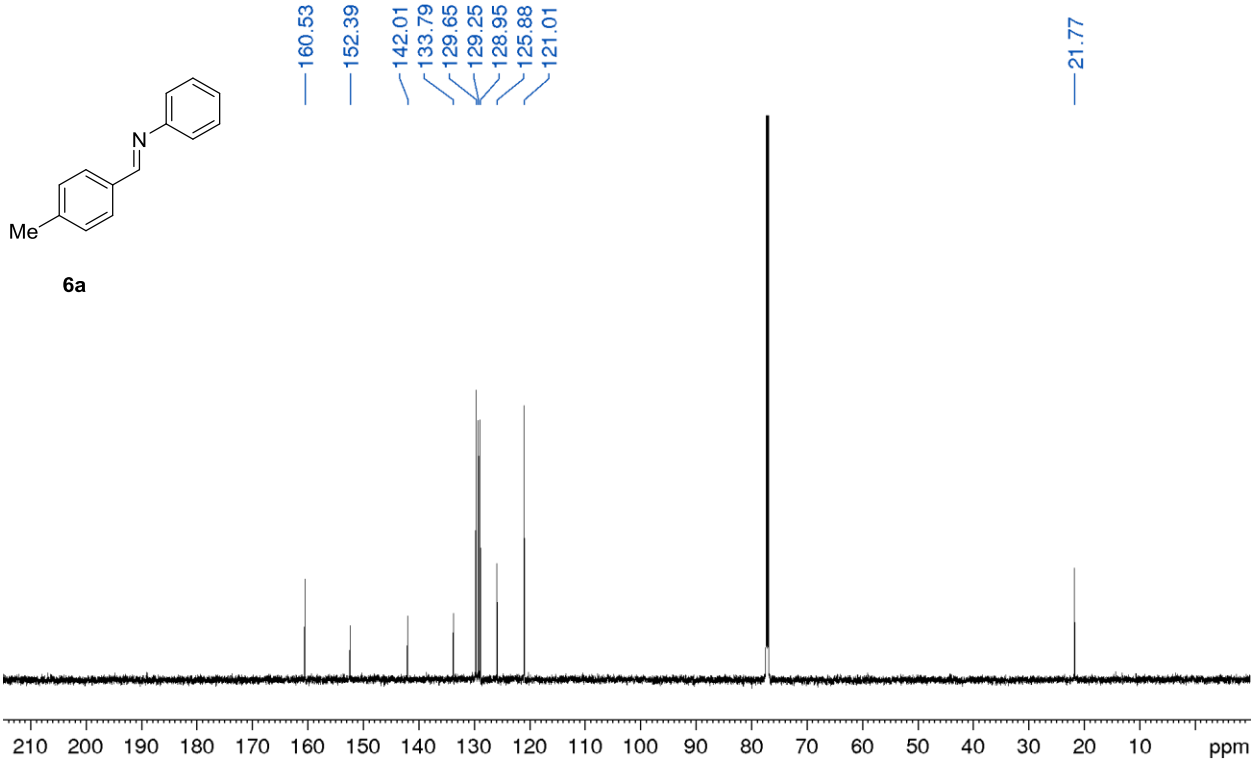



$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6a**

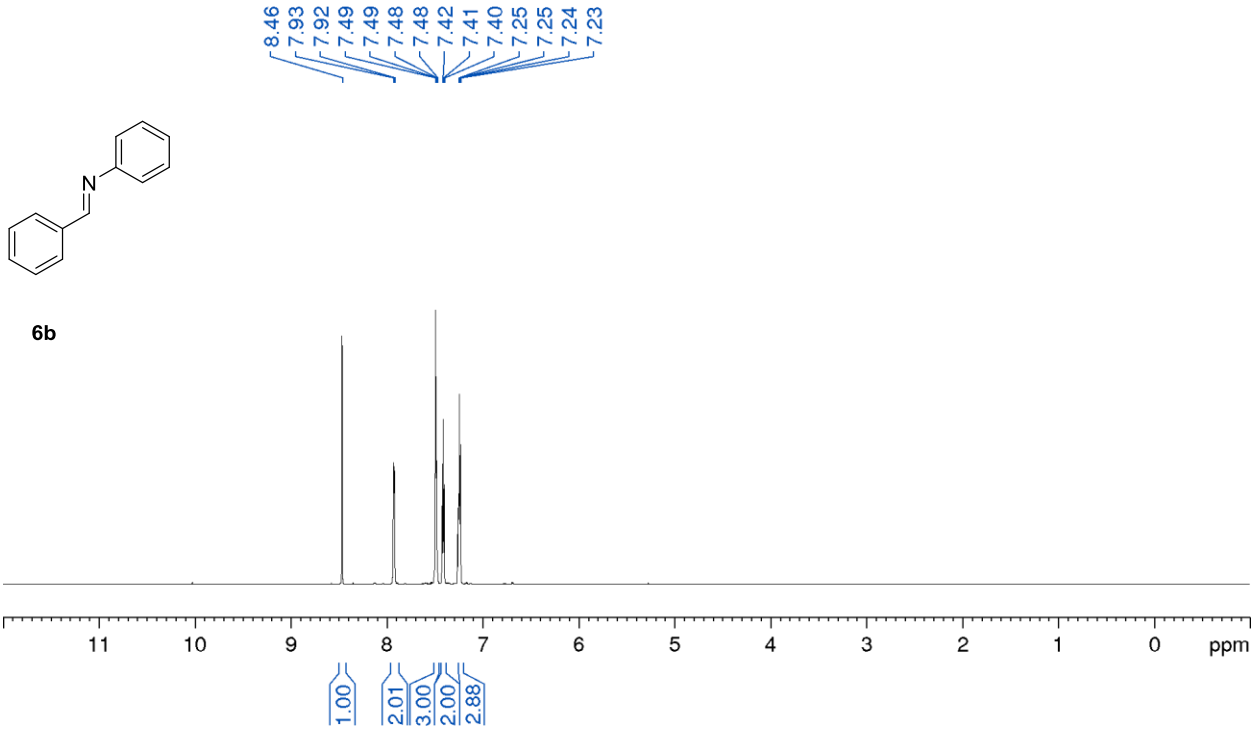



**6a**

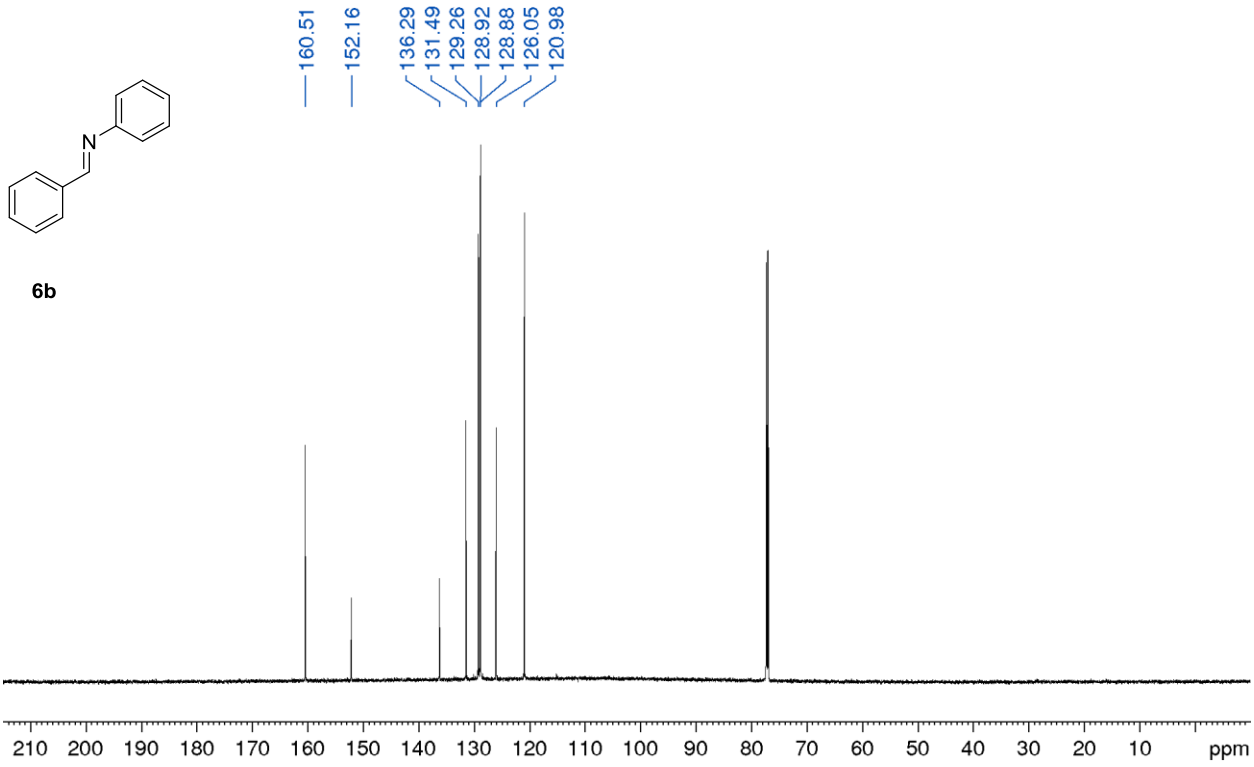
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6a**



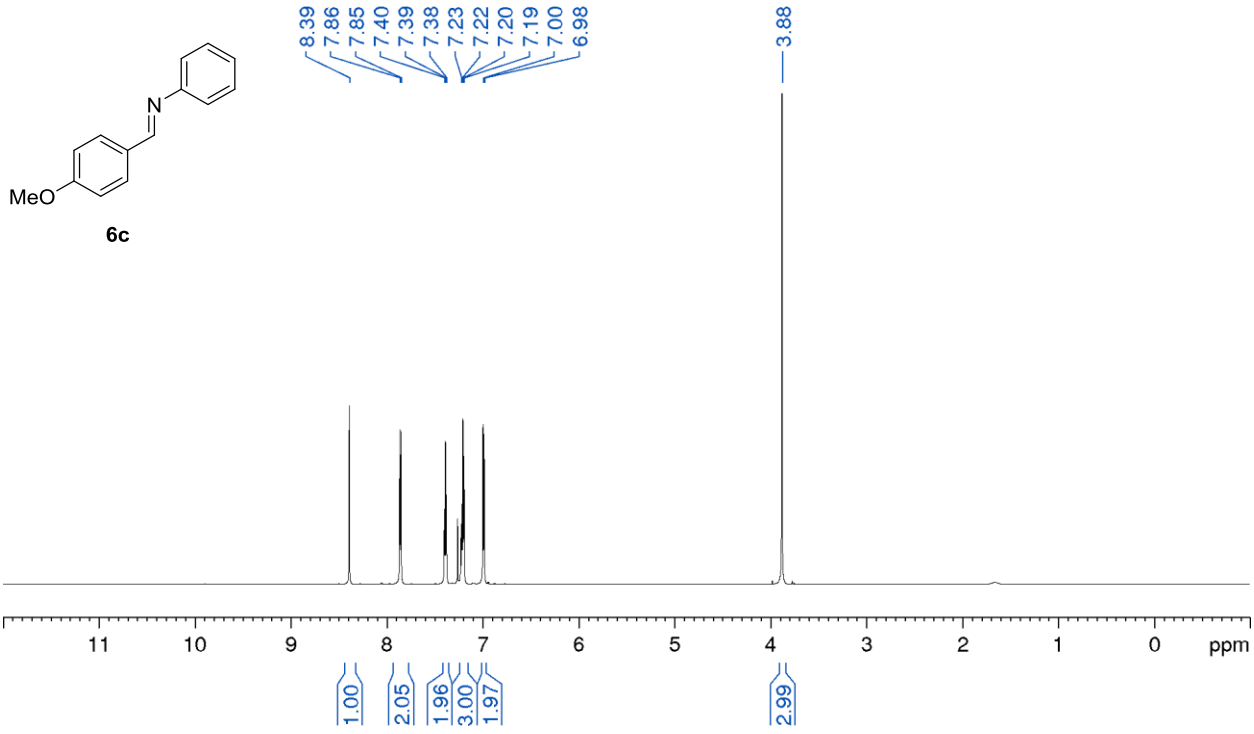

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6b**



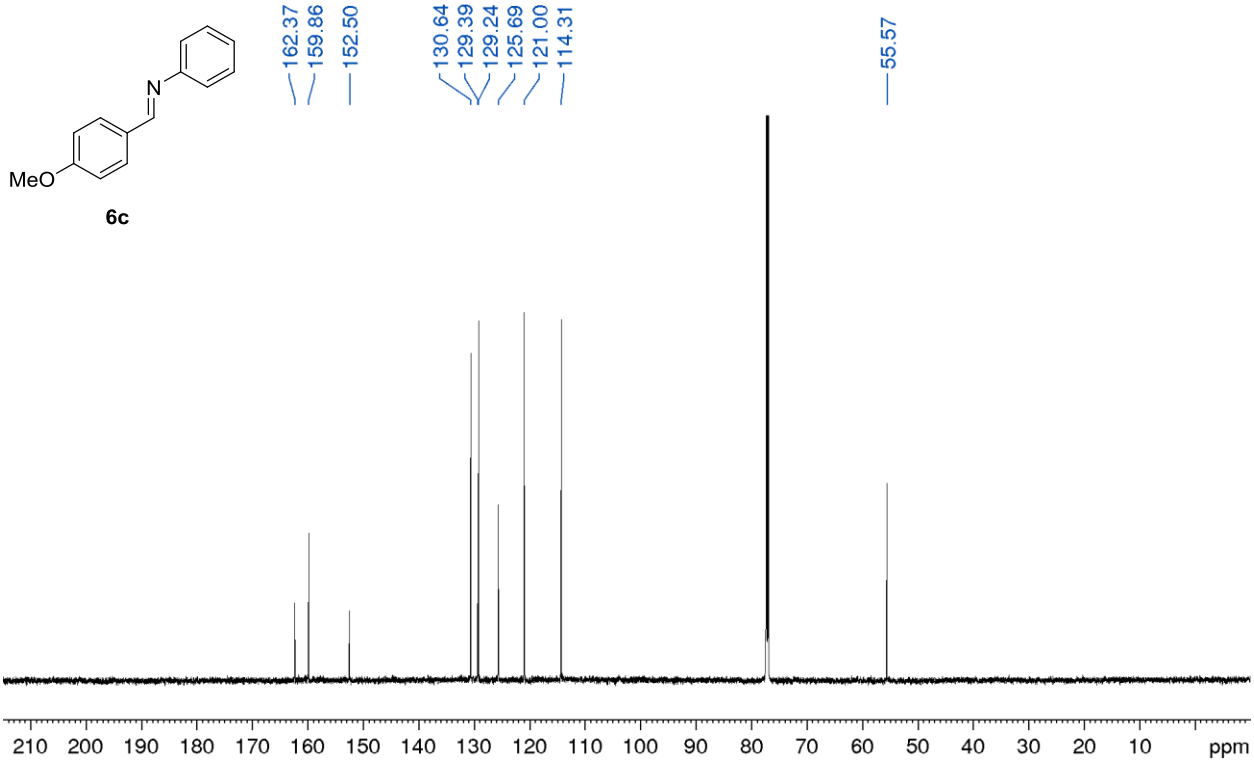
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6b**



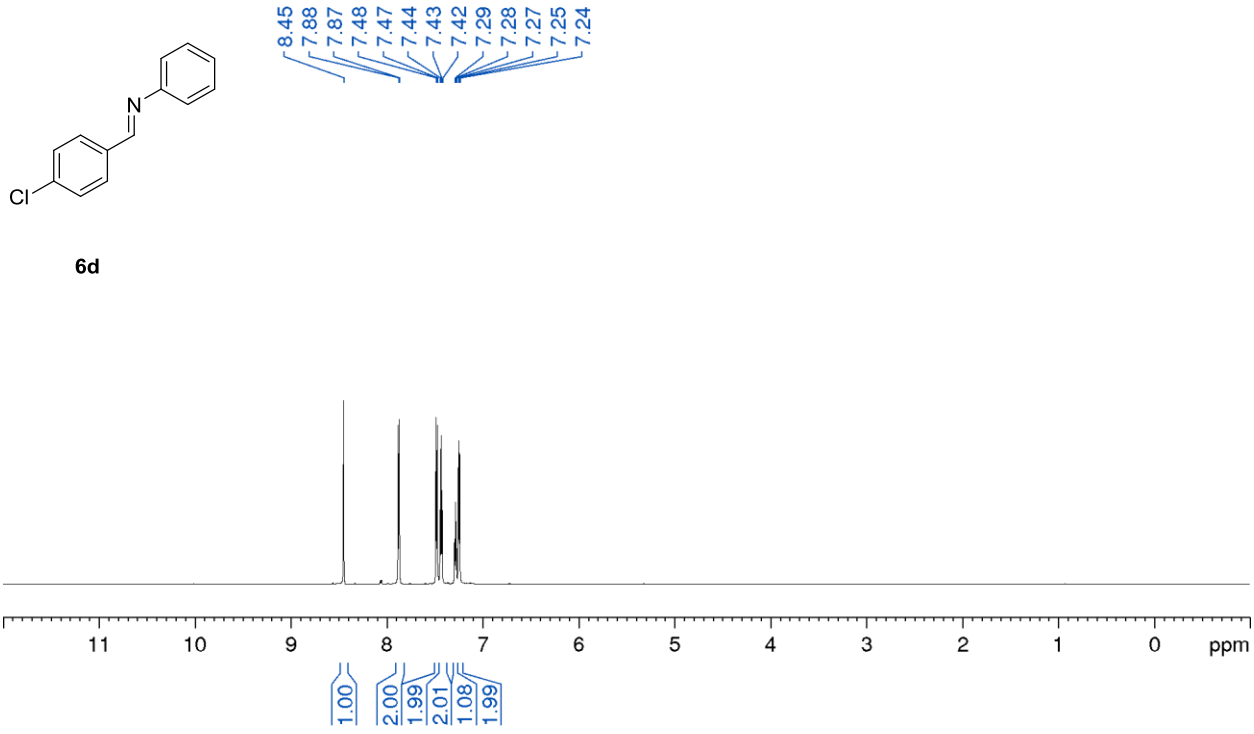

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6c**



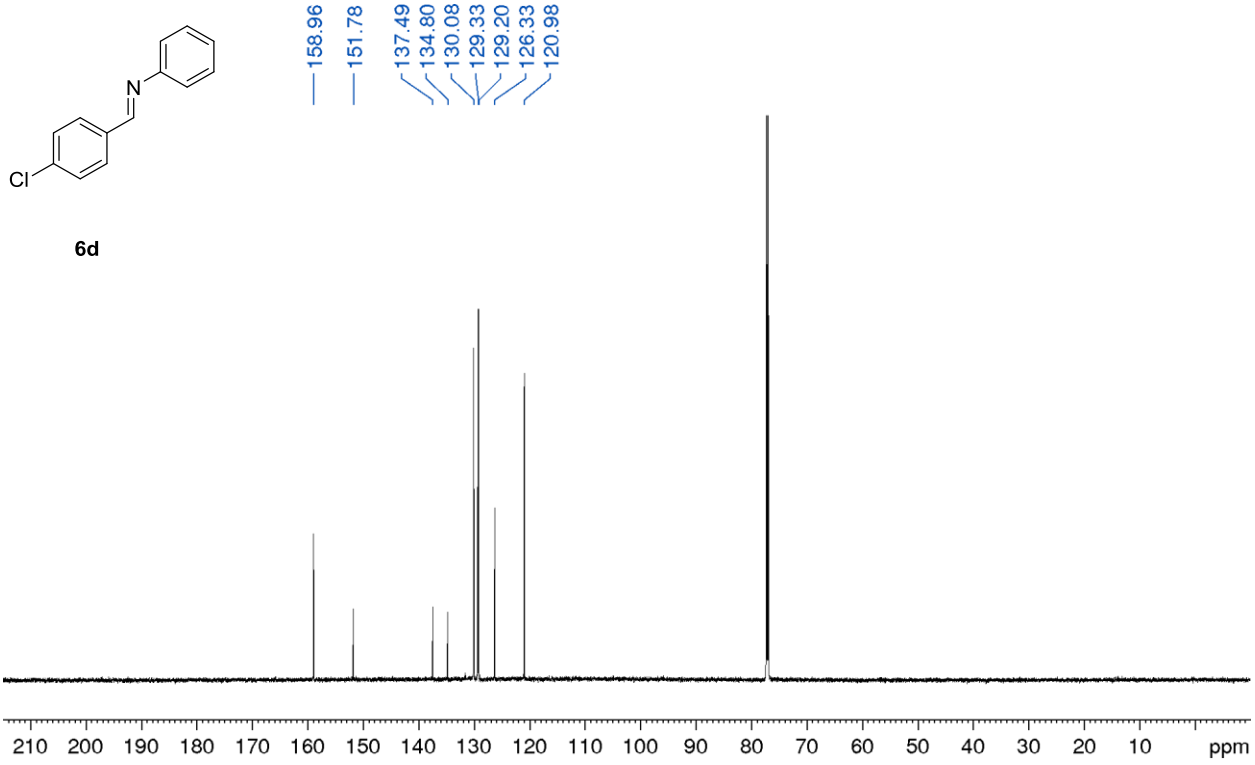
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6c**



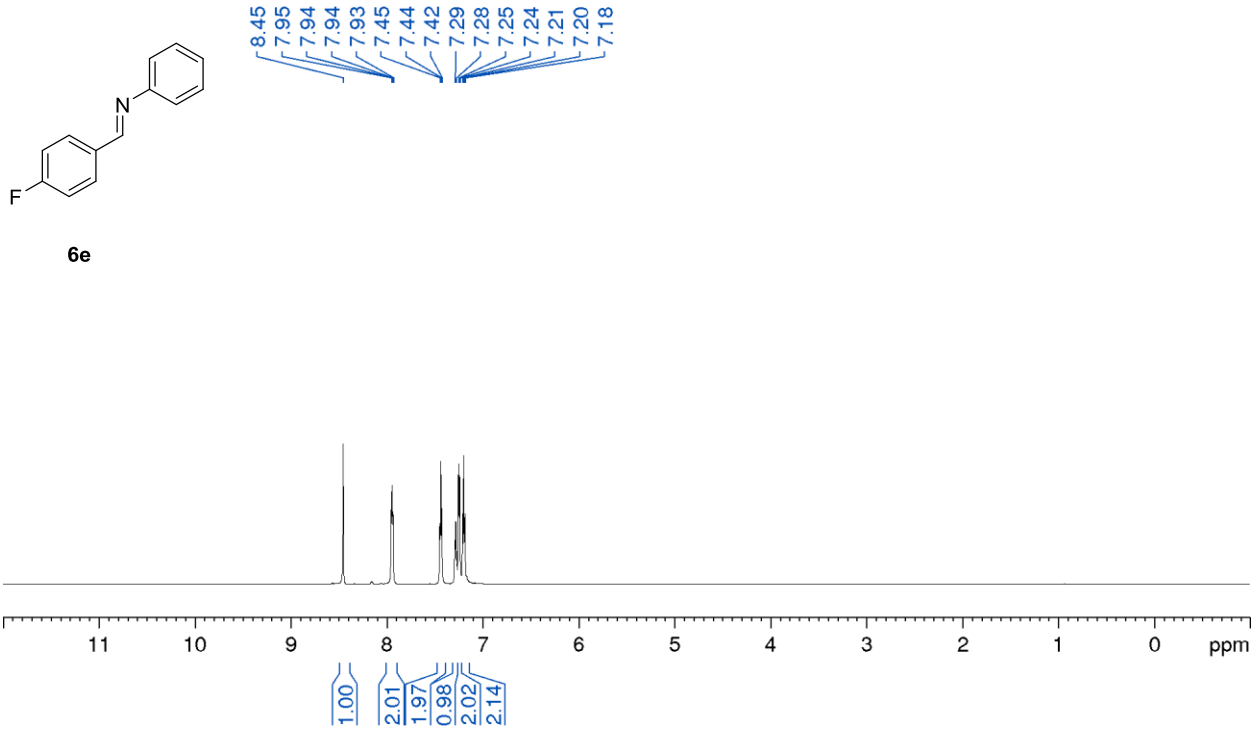

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6d**



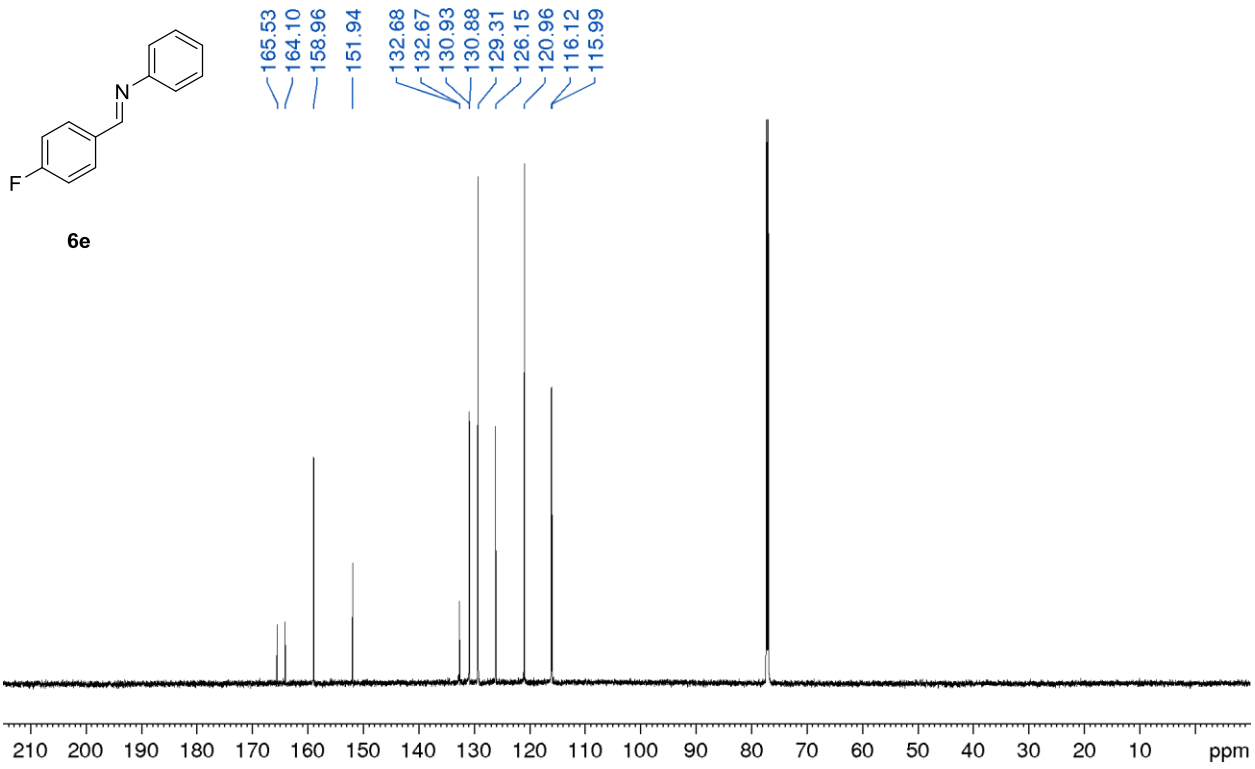
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6d**



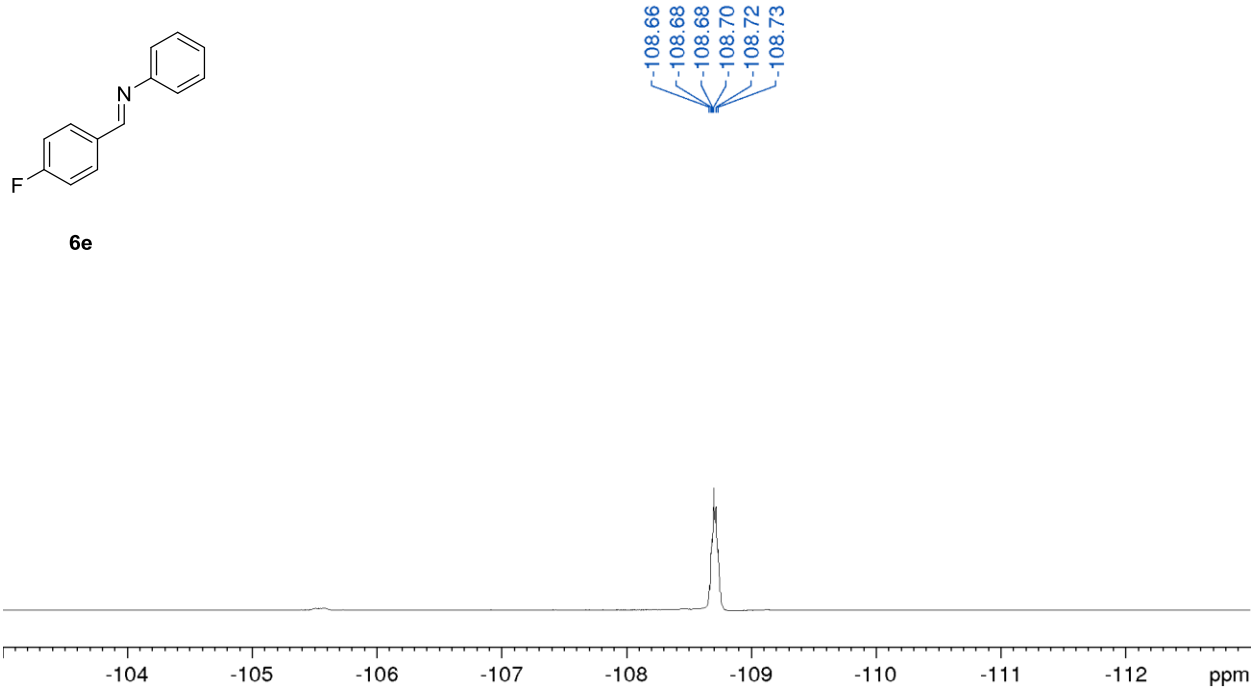

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6e**



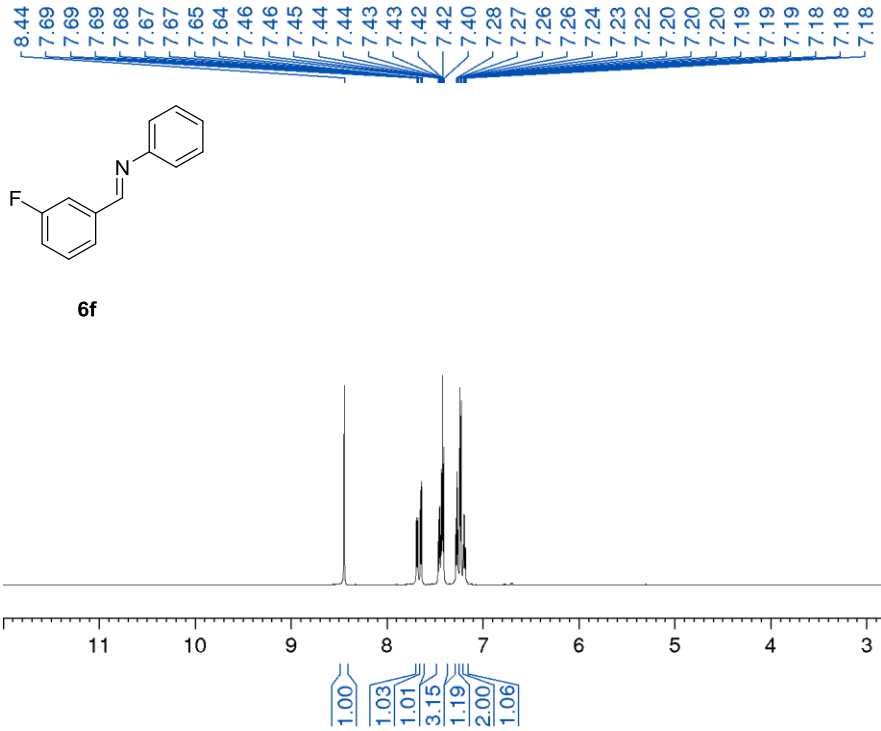
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6e**




$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **6e**

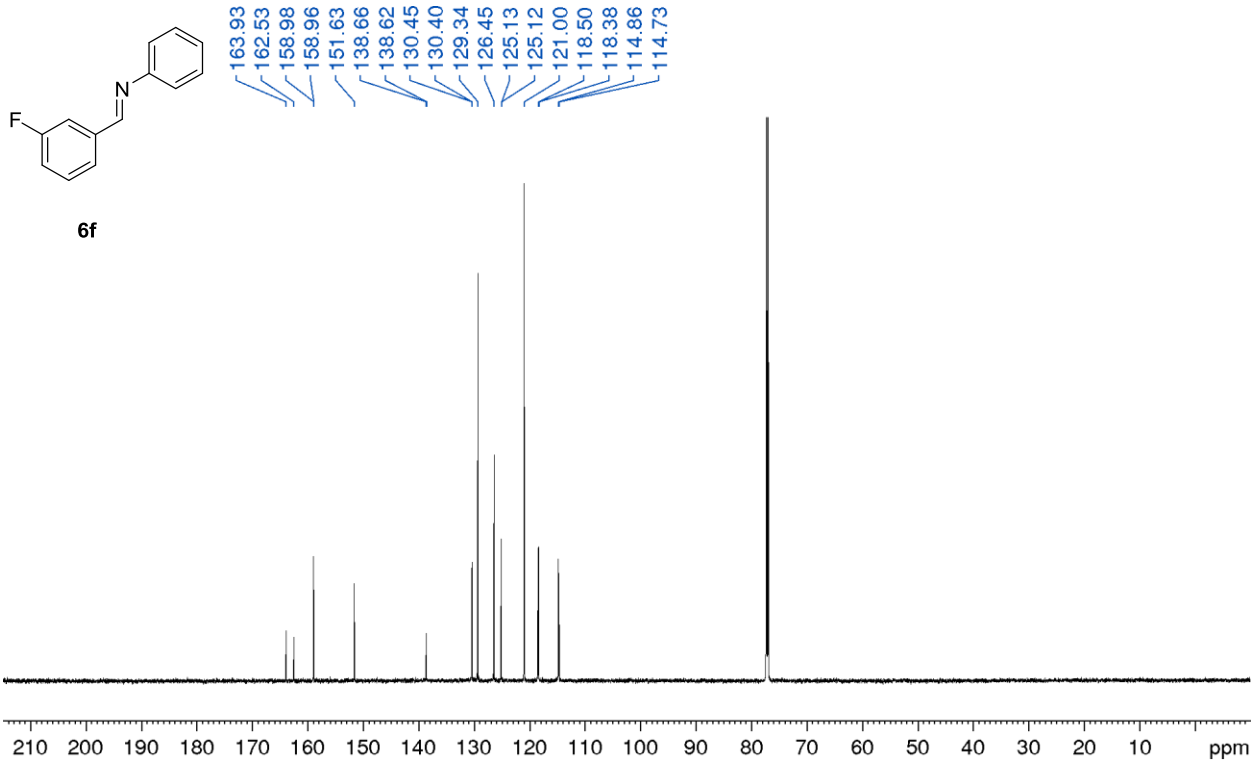


$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **6f**



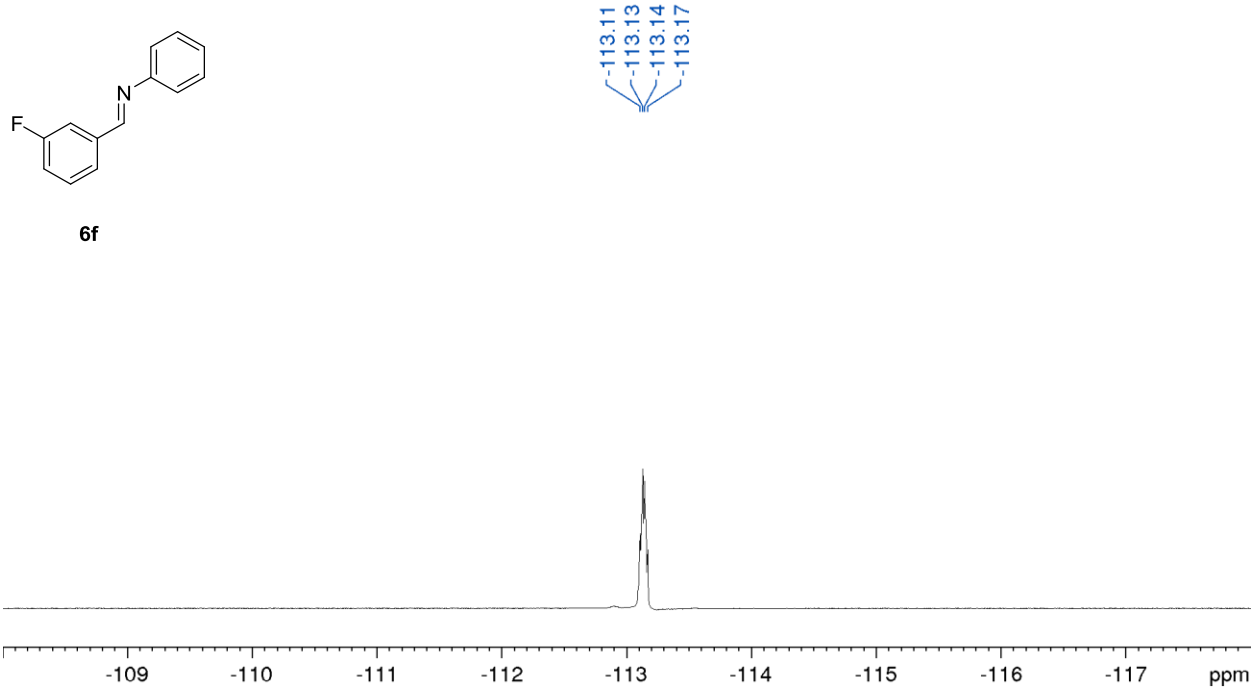

**6f**

$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **6f**



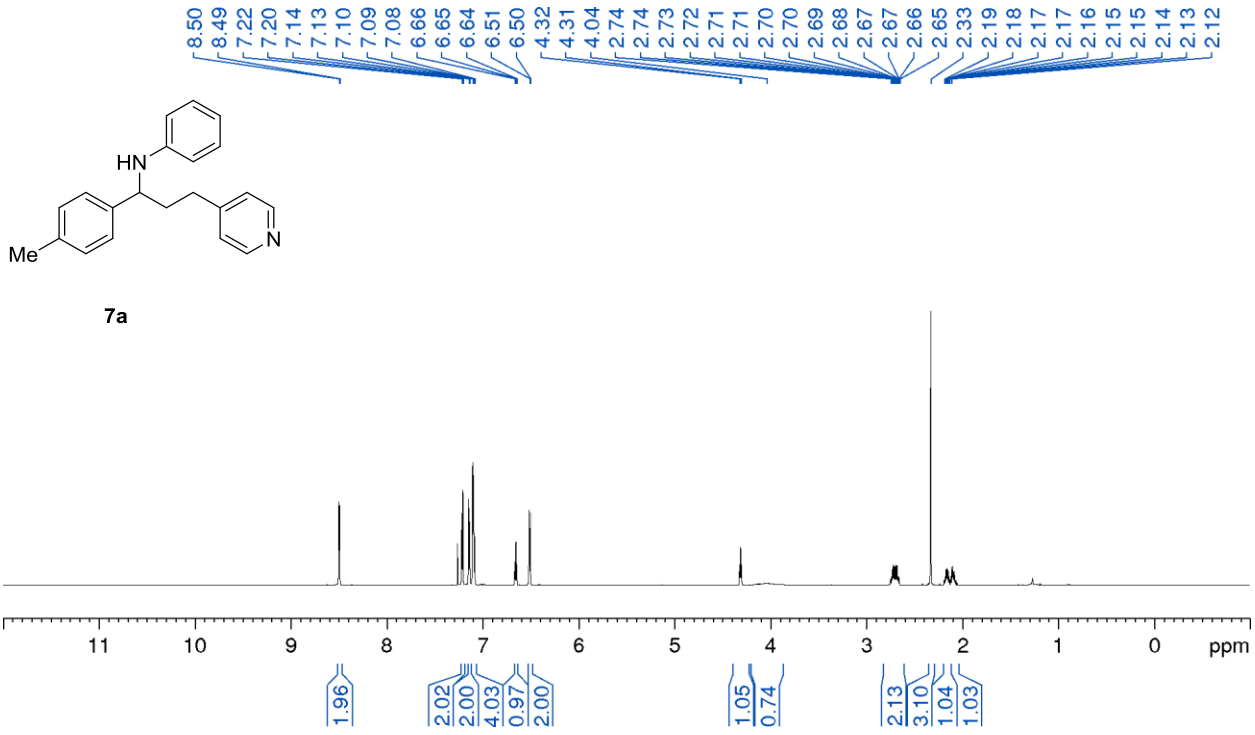

**6f**

$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **6f**



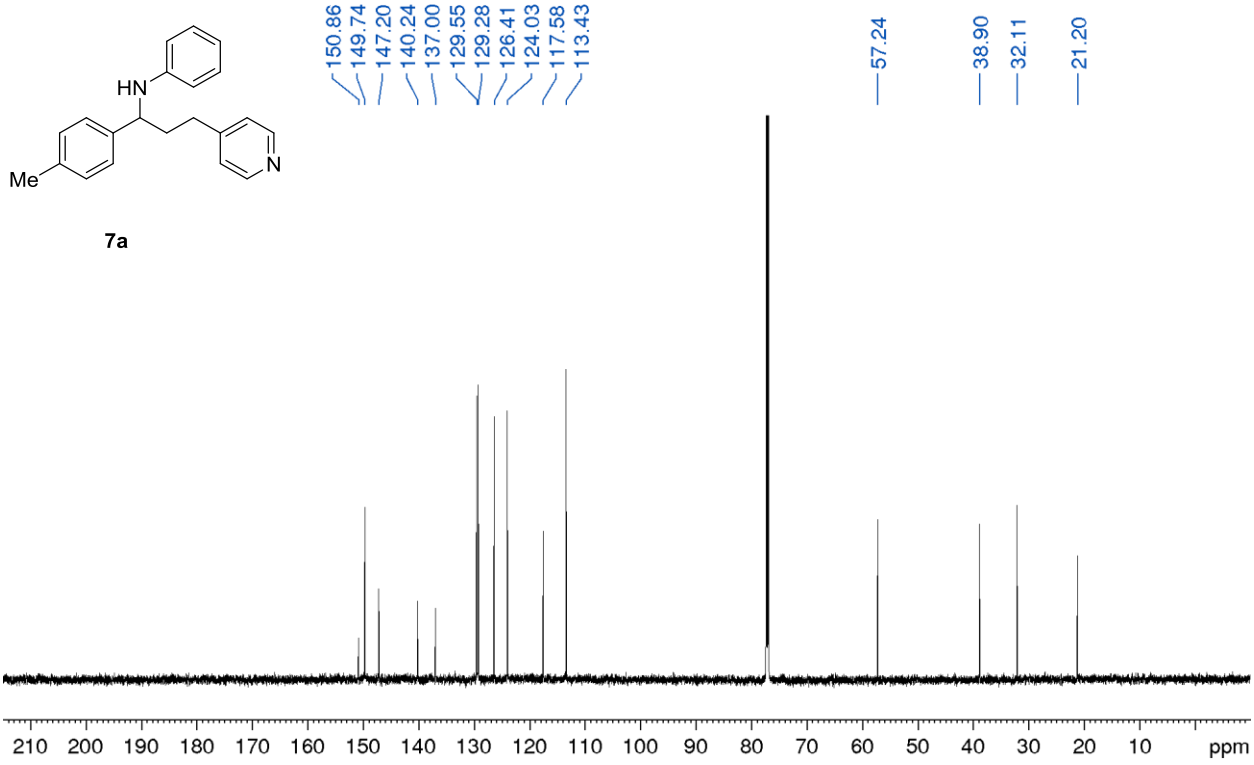

**6f**

$^{1}$H NMR (700 MHz, $CDCl_3$, 25 ºC) of **7a**

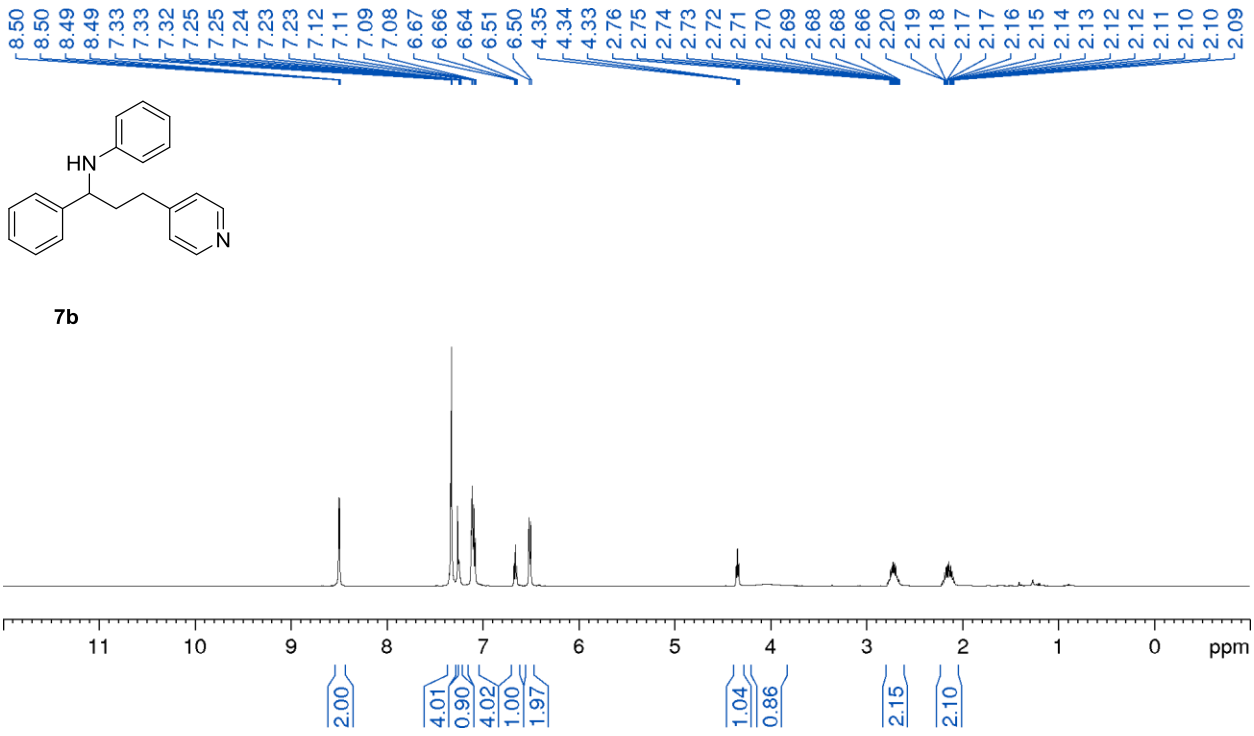



**7a**

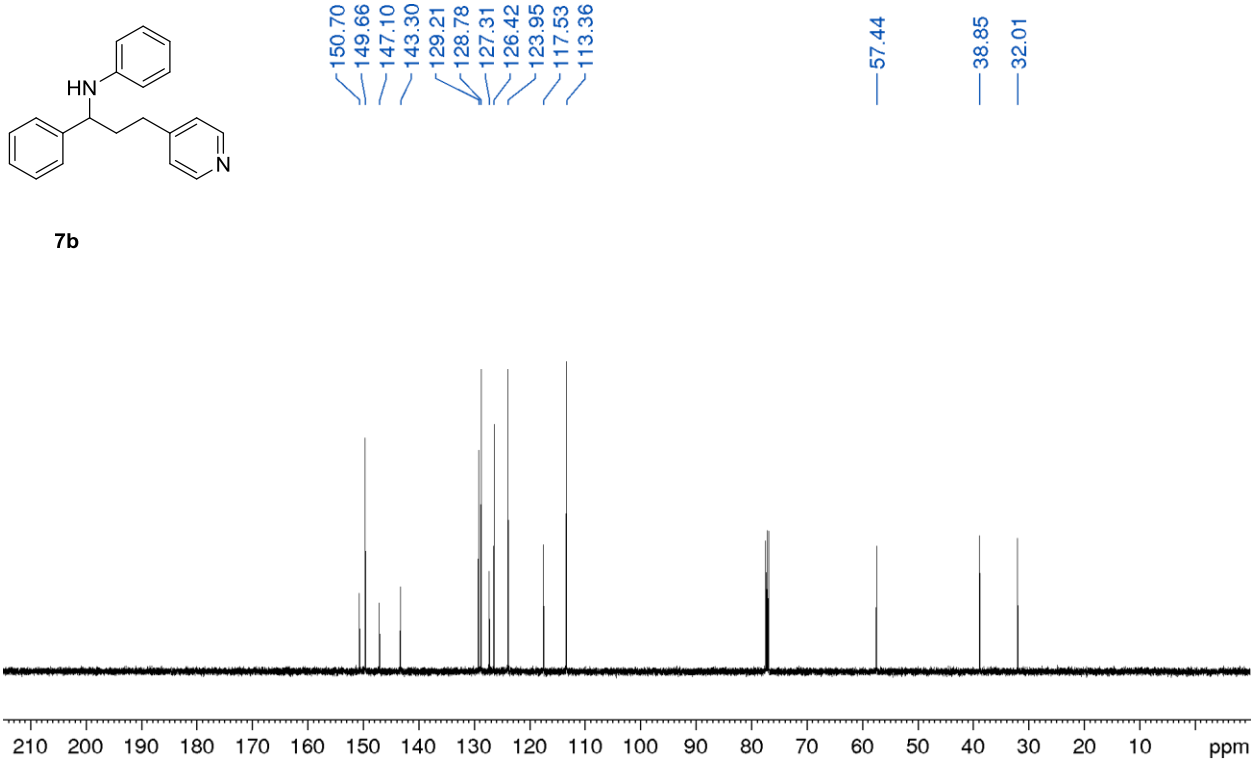
$^{13}$C NMR (176 MHz, $CDCl_3$, 25 ºC) of **7a**




$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **7b**

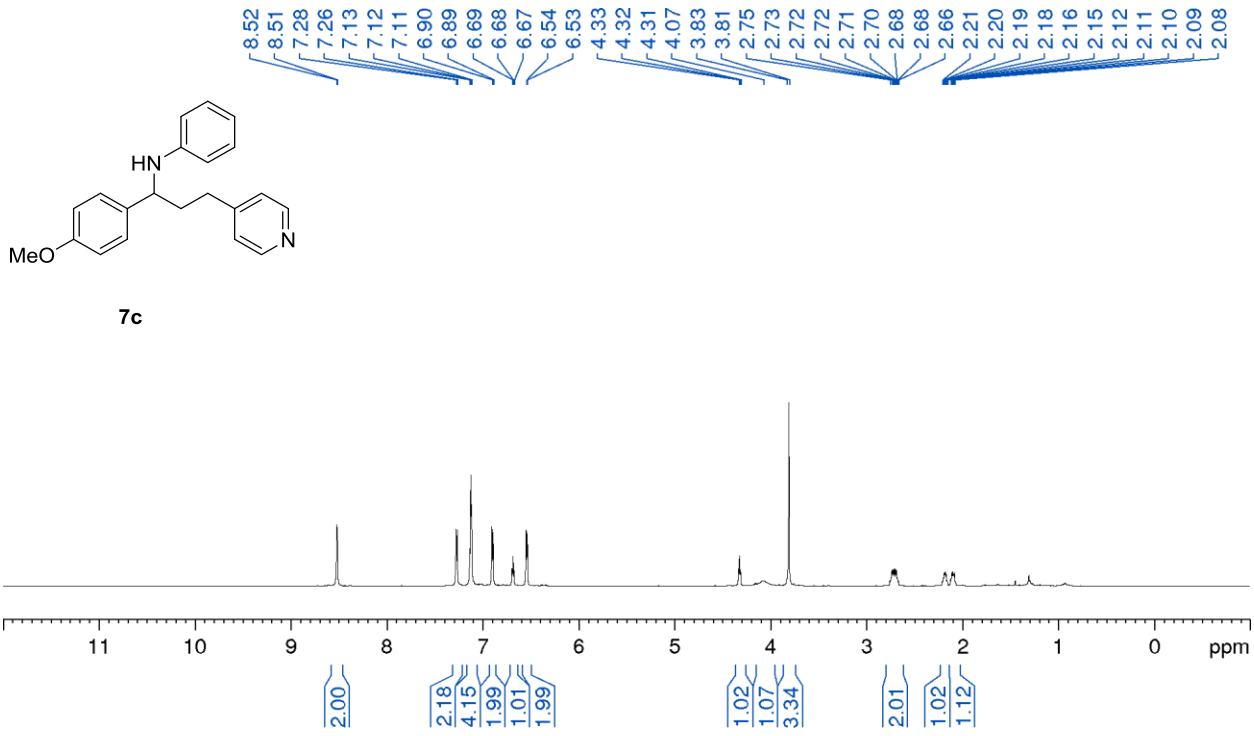


$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **7b**



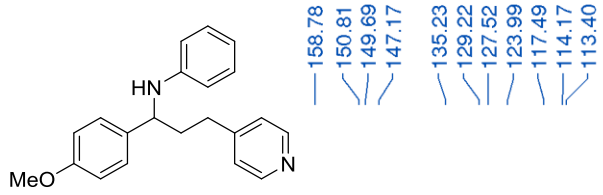

**7b**

$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **7c**




**7c**

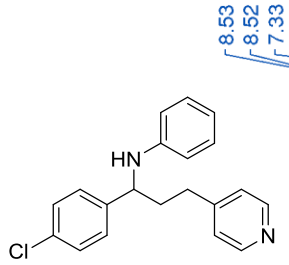
$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **7c**




**7c**

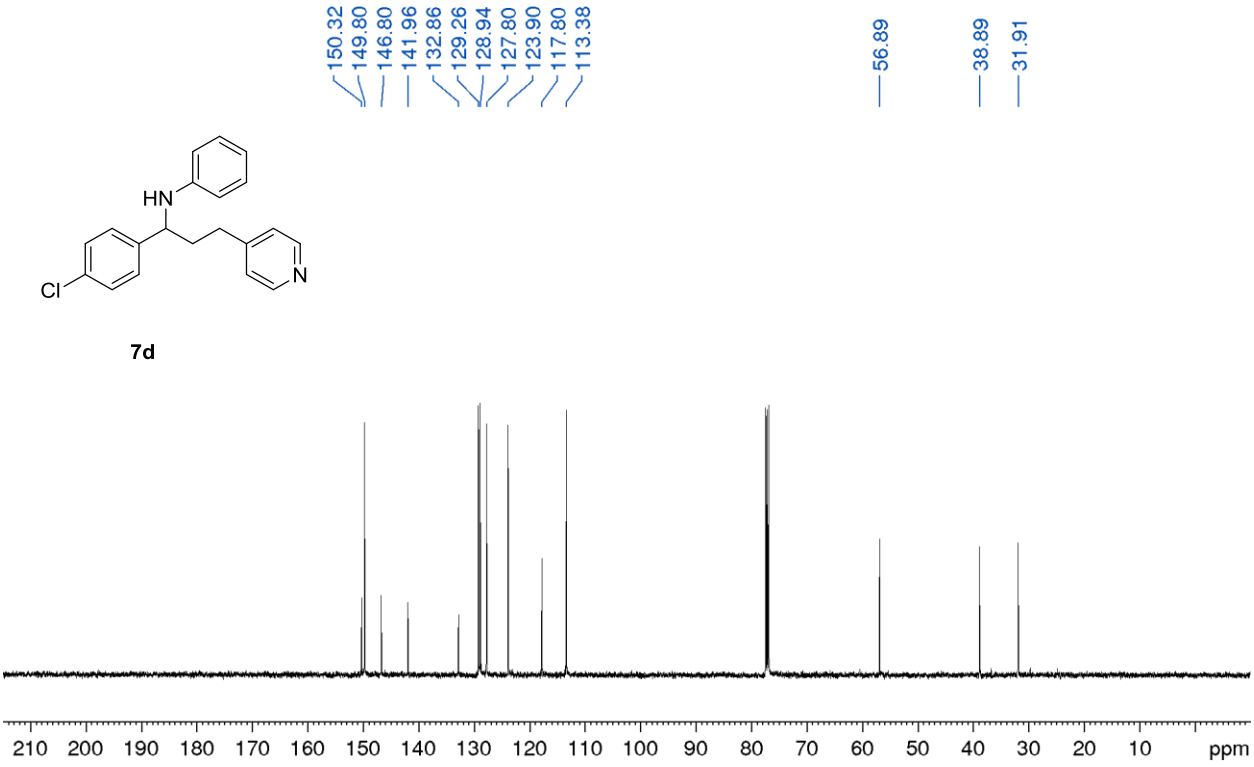



$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **7d**



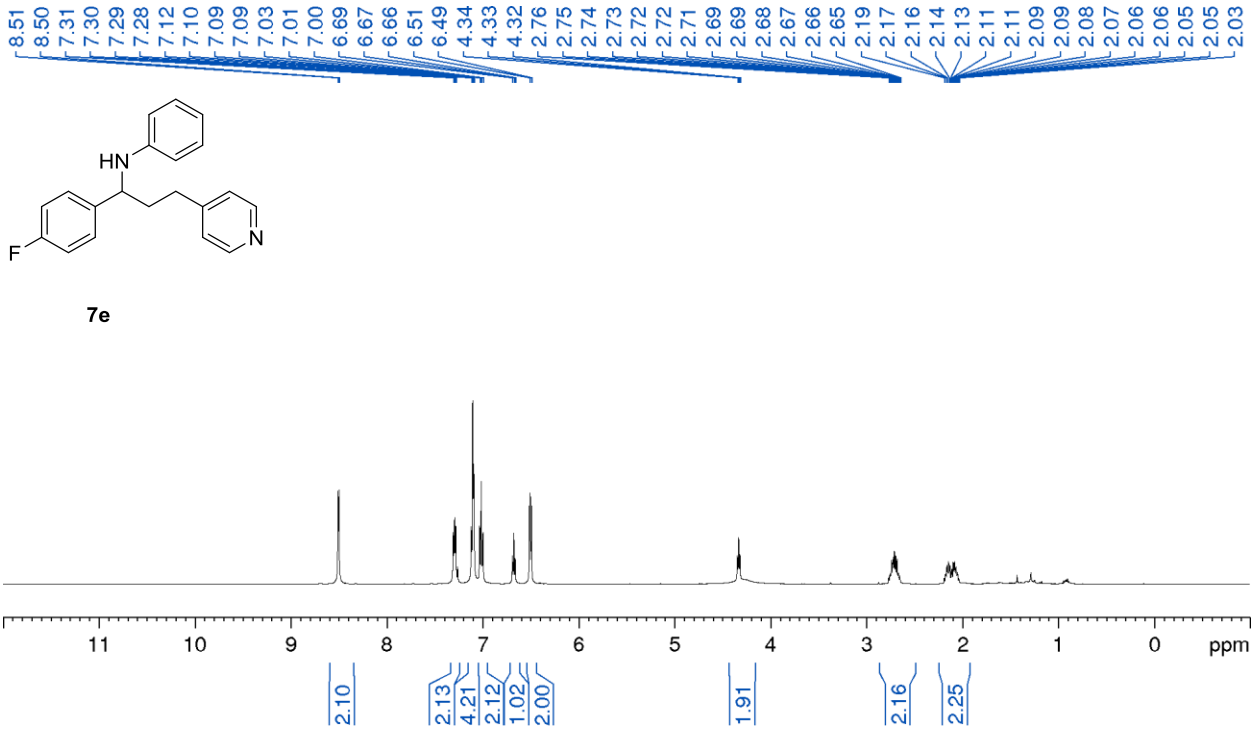

**7d**

$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **7d**



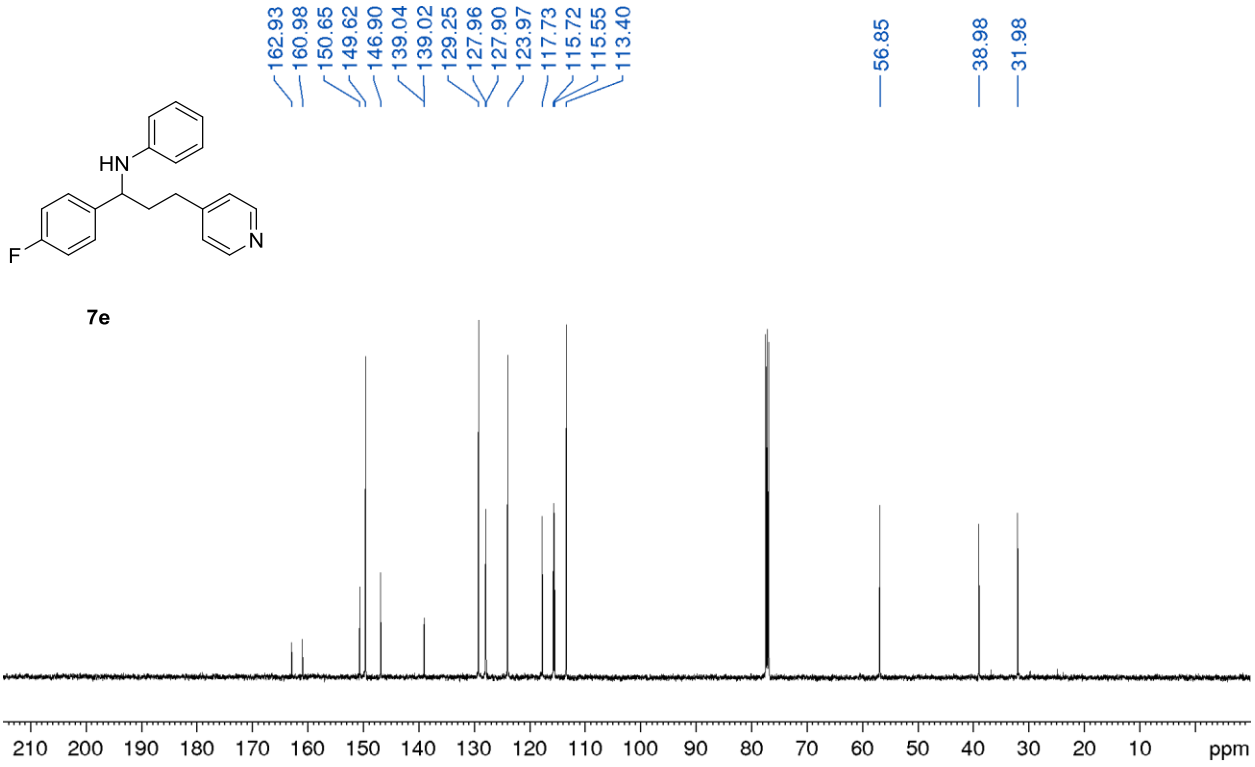

**7d**

$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **7e**

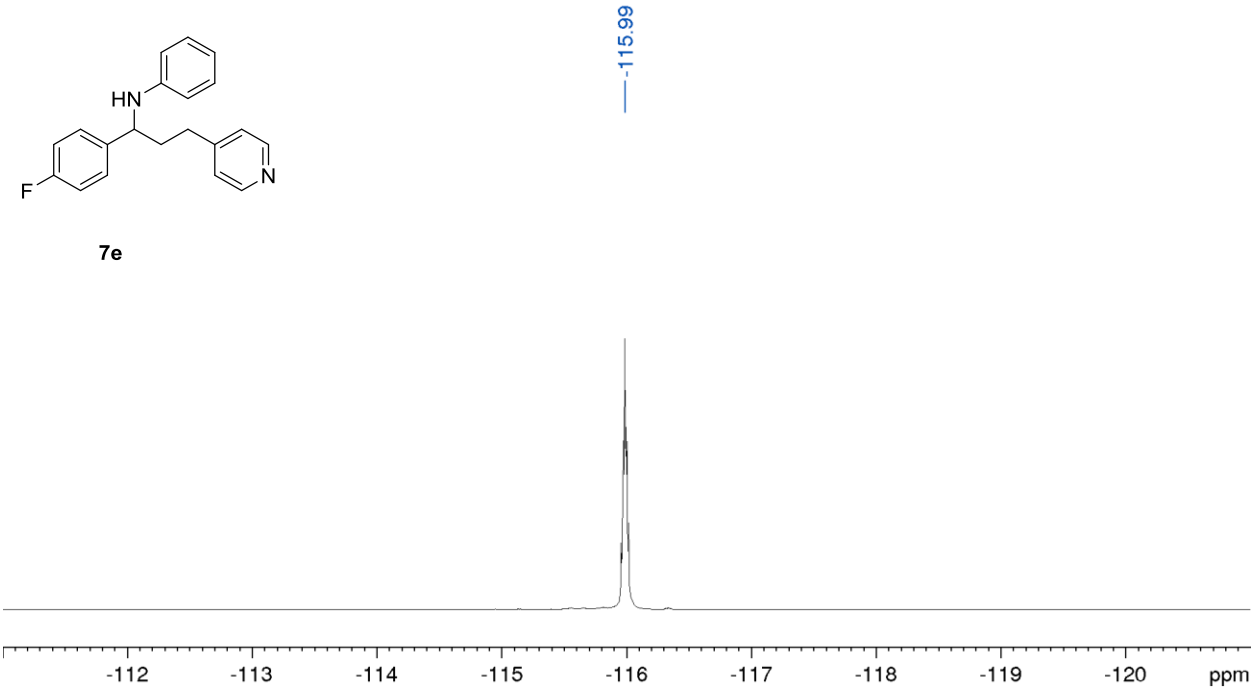



**7e**

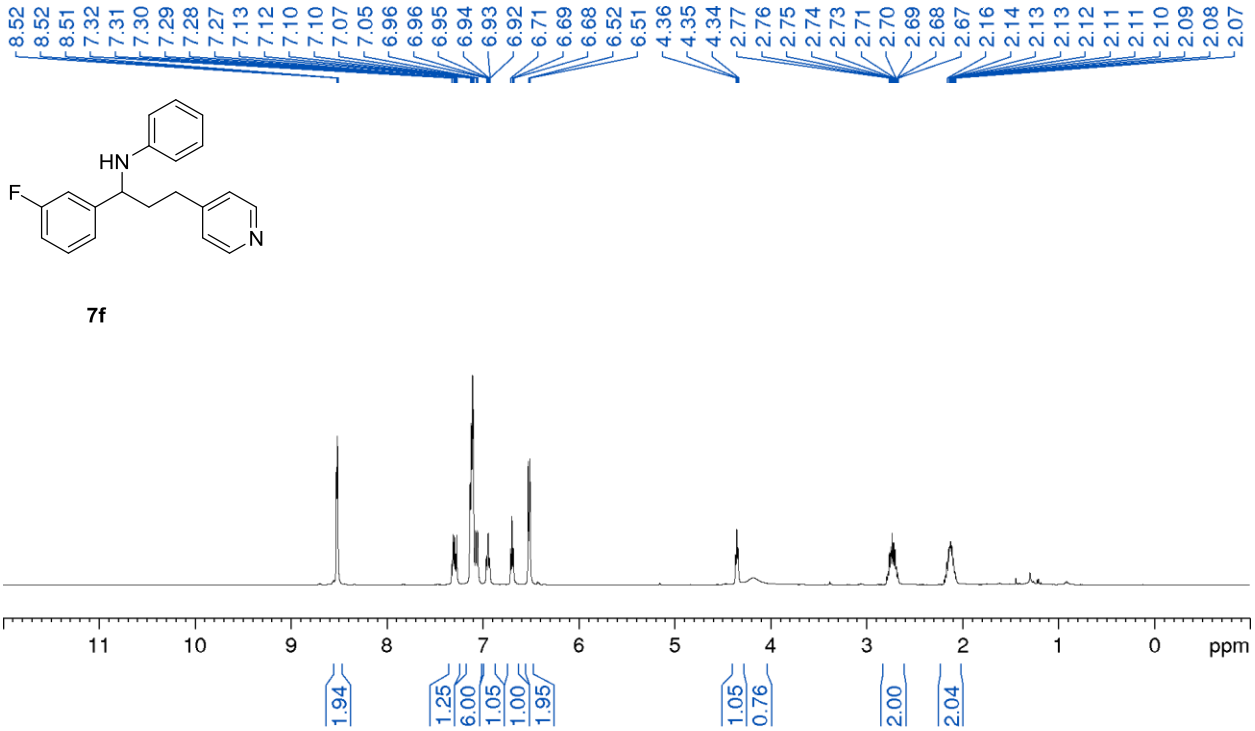
$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **7e**




$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **7e**

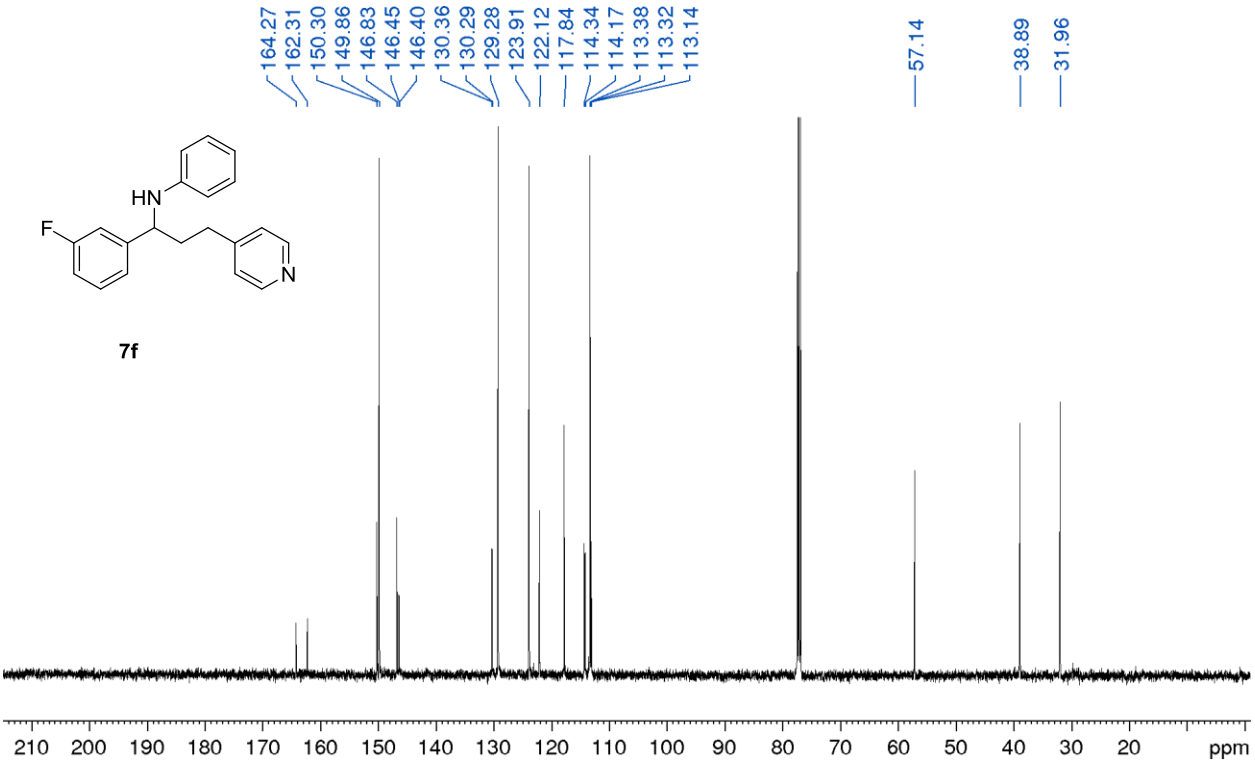


$^{1}$H NMR (500 MHz, $CDCl_3$, 25 ºC) of **7f**



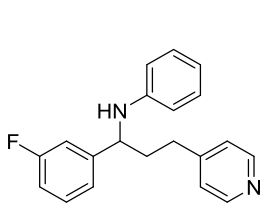

**7f**

$^{13}$C NMR (125 MHz, $CDCl_3$, 25 ºC) of **7f**




**7f**

$^{19}$F NMR (376 MHz, $CDCl_3$, 25 ºC) of **7f**




**7f**

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