Supplementary Information

Skeletal Editing of Pyrimidines to Pyrazoles by Formal Carbon Deletion

G. Logan Bartholomew, Filippo Carpaneto, and Richmond Sarpong*

Department of Chemistry, University of California, Berkeley, CA, 94720, US

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1. General Considerations for Chemical Synthesis

i) Solvents and Reagents

Tetrahydrofuran (THF), toluene (PhMe), benzene (PhH), methanol (MeOH), acetonitrile (MeCN), and triethylamine (Et_3N) were purchased from Fisher Scientific and then sparged with argon and dried by passing through alumina columns using argon in a Glass Contour SPS prior to use. Dichloromethane (CH_2Cl_2) was obtained from Fisher Scientific and freshly distilled over calcium hydride under an atmosphere of nitrogen prior to each use. 1,2- Dichloroethane (DCE), 1,2-dimethoxyethane (DME), chloroform ($CHCl_3$), and chlorobenzene (PhCl), and 1,4-dioxane were purchased from Sigma Aldrich in 1 L SureSeal® bottles and used as received. Reagents were purchased from commercial vendors as follows: hydrazine (98%), hydrazine hydrochloride (98%), 4-chloro-6-methylpyrimidine (97%), 4'-aminoacetophenone (99%), 4-aminopyrimidine (95%), 4,6-dihydroxypyrimidine (99%), pyridine (99%, Sure/Seal®), Fenarimol® (99.5%), Bis(triphenylphosphine)palladium(II) dichloride (99%, trace metal basis), tBuXPhos Pd G3 (99%, trace metal basis), phenylhydrazine hydrochloride (99%), phenylhydrazine (97%), 4'methoxyphenylhydrazine hydrochloride (98%), 3'bromophenylhydrazine hydrochloride (98%), benzohydrazide (99%) were purchased from Sigma Aldrich; triflic anhydride (98%), sodium carbonate (99%, trace metal basis), potassium carbonate (99%, trace metal basis), cesium carbonate (99%, trace metal basis), DABCO (95%), DBU (98%), zinc (II) triflimide (99%, trace metal basis), Tongi's reagent (98%), Umemoto's reagent (99%), 6-bromoquinazoline (95%), and 2'-Bromoacetophenone (98%) were purchased from Fisher Scientific; 2-((4-Chloropyrimidin-5-yl)oxy)-5-fluoro-N,N-diisopropylbenzamide (98%), phenylboronic acid (98%), 4'-dimethylaminophenylboronic acid (95%), 4'-methoxyphenylboroni acid (99%), and pyridine-3-boronic acid pinacol ester (95%) were purchased from Combi-Blocks; 4-benzyloxy-3-fluorophenylboronic acid (98%) and 2-chloro-4-phenyl-pyrimidine (95%) were purchased from Ambeed; triflic anhydride (95%) was purchased from Oakwood chemical.

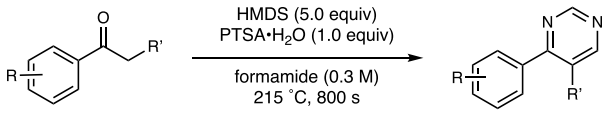
ii) Experimental Procedures

Unless otherwise noted in the experimental procedures, reactions were carried out in flame-dried glassware under a positive pressure of N_2 in anhydrous solvents using standard Schlenk techniques. Reaction temperatures above room temperature (22–23 °C) were heated using silicone oil or sand baths controlled and monitored by an IKA® temperature modulator. Reaction progress was monitored using thin-layer chromatography (TLC) on SiliCycle Siliaplates (glass backed, extra hard layer, 60 Å, 250 µm thickness, F254 indicator). Visualization of the developed plates was performed under UV-light (254 nm) irradiation, and then gently heated with potassium permanganate ($KMnO_4$) or phosphomolybdic acid (PMA) stain. Flash column chromatography employed SiliaFlash P60 silica gel purchased from SiliCycle Inc. Automated flash chromatography was performed using a Yamazen Smart Flash EPCLC W-Prep 2XY (dual channel) system on prefilled, premium, universal columns using ACS grade solvents. NMR yields were acquired using ethylene carbonate (^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 4H)) as the internal standard.

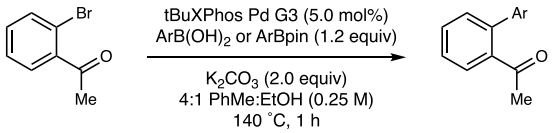
iii) Analytical Instrumentation

^{1}H NMR and ^{13}C NMR data were recorded on Bruker AVQ-400, AVB-400, AV-500, AV-600, and NEO-500 MHz spectrometers using $CDCl_3$, C_6D_6, or $(CD_3)_2SO$ as solvents, typically at 20–23 °C. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ 7.26 for ^{1}H NMR, δ 77.16 for ^{13}C NMR in $CDCl_3$; δ 7.16 for ^{1}H NMR, δ 128.06 for ^{13}C NMR in C_6D_6; δ 2.50 for ^{1}H NMR, δ 39.52 for ^{13}C NMR in $(CD_3)_2SO$)). Data for ^{1}H NMR spectroscopy are reported as follows; chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, hept = heptet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C spectroscopy are reported in terms of chemical shift (δ ppm). *Note: The AV-500 and AV-600 instruments are partially supported by NIH grants SRR023679A and 1S10RR016634-01. The CRYO-900 instrument is funded by NIH grant GM68933.* Melting points were determined using a MEL-TEMP™ apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. High-resolution mass spectra (HRMS) were obtained at the Catalysis Center at the University of California, Berkeley on a Bruker ALPHA FT-spectrometer and reported in cm^{-1}. Samples are loaded onto the diamond surface either neat or as a solution in organic solvent and the data was acquired after the solvent had evaporated.

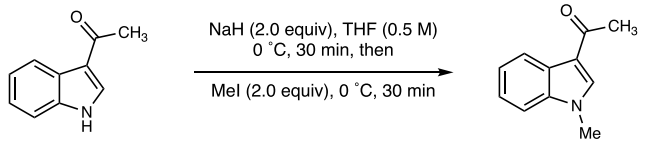
2. Synthetic Procedures and Product Characterization



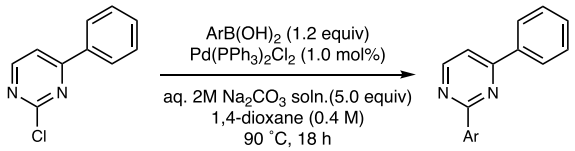
***General Procedure A* for the synthesis of 4-arylpyrimidines.** Prepared according to a previously reported protocol.[1] To a 20 mL sealable microwave vial was added an oven-dried stir bar, ketone (1.0 equiv), formamide (0.3 M), hexamethyldisilazane (5.0 equiv), and *p*-toluenesulfonic acid monohydrate (1.0 equiv). The vial was sealed using a crimp cap. The resulting biphasic mixture was subjected to microwave irradiation at 215 ˚C for 800 s with 600 rpm stirring using a Biotage® Initiator+ microwave synthesizer. The reaction mixture was allowed to cool and was then loaded onto a 2-inch plug of silica. The silica plug was washed with acetone (20 mL), and the filtrate was concentrated *in vacuo*. The crude residue was purified by flash column chromatography (hexanes:acetone).



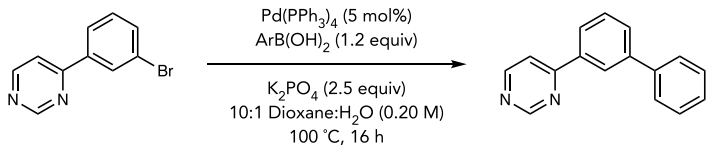
***General Procedure B* for the synthesis of 2'-aryl acetophenones.** To a 5 mL sealable microwave vial equipped with a stir bar was added 2'-bromoacetophenone (1.0 equiv), aryl boronic acid or aryl pinacol borane (1.2 equiv), K_2CO_3 (2.0 equiv), tBuXPhos Pd G3 (5.0 mol%), and 4:1 PhMe:EtOH (0.25 M) under air at 23 °C. The vial was sealed with a crimp-top septum and evacuated and backfilled thrice with nitrogen. The resulting mixture was heated to 140 °C by microwave irradiation and allowed to stir at that temperature for 1 h. Upon completion of the reaction as judged by TLC (8:2 hexanes:acetone, UV visualization), the mixture was allowed to cool to 23 °C. The mixture was taken into a pipette and passed through a short bed of Celite. The resulting filtrate was concentrated *in vacuo*, and the resulting crude residue was purified by flash column chromatography (hexanes:acetone) to give the desired 2-arylated-acetophenones.



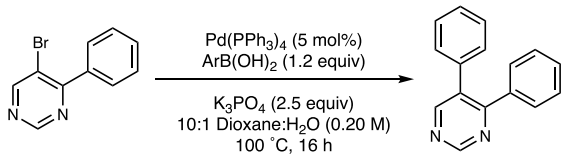
1-(1-methyl-1*H*-indol-3-yl)ethan-1-one. Prepared according to a previously-reported protocol.[2] To a flame-dried 50 mL round-bottomed flask under nitrogen atmosphere at 23 °C was added 3-acetylindole (1.0 g, 6.3 mmol, 1.0 equiv) and anhydrous THF (13 mL, 0.5 M). The resulting mixture was cooled to 0 °C, after which NaH (60% dispersion in mineral oil, 0.50 g, 12.6 mmol, 2.0 equiv) was added portion-wise against a backflow of nitrogen. The resulting mixture was allowed to stir at 0 °C for 30 min, after which methyl iodide (0.80 mL, 12.6 mmol, 2.0 equiv) was added dropwise at 0 °C. The resulting mixture was allowed to stir at 0 °C for 30 min, after which the solvent was removed *in vacuo* and the resulting crude concentrate was suspended in EtOAc (30 mL). The resulting suspension was cooled to 0 °C, and water (20 mL) was added dropwise to quench any remaining NaH. After stirring the resulting mixture at 0 °C for 20 min, the phases were separated, and the organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo* to yield a yellow solid. The solid mass was triturated with hexanes (20 mL) and dried under vacuum to yield the title compound as a pale-yellow solid (1.2 g, 100%).



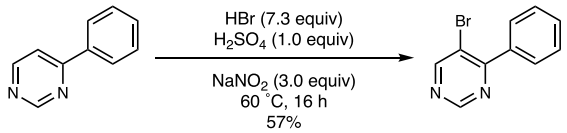
***General Procedure C* for the synthesis of 2,4-diaryl pyrimidines.** To an oven-dried 15 mL screw-top vial with PTFE-lined threads was added 2-chloro-4-phenyl pyrimidine (200 mg, 1.0 mmol, 1.0 equiv), aryl boronic acid (1.2 mmol, 1.2 equiv), and $Pd(PPh_3)Cl_2$ (7.1 mg, 0.010 mmol, 1.0 mol%). The vial was capped with a rubber septum, evacuated and backfilled with nitrogen thrice before a 2 M aqueous solution of Na_2CO_3 (2.5 mL, 5.0 equiv) and 1,4-dioxane (2.5 mL) were added at 23 ˚C. The rubber septum was replaced with a PTFE-lined cap against a nitrogen backflow. The resulting mixture was brought to 90 ˚C and allowed to stir at that temperature for 18 h. The resulting mixture was allowed to cool to 23 ˚C and then passed through a short plug of Celite and concentrated *in vacuo*. The crude residue was purified by flash column chromamtography (hexanes:acetone) to give the desired 2-arylated pyrimidines.



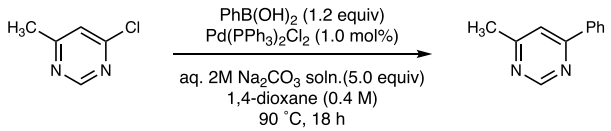
4-([1,1'-biphenyl]-3-yl)pyrimidine. To a 15 mL screw top vial equipped with a stir bar was added 4-(3-bromophenyl)pyrimidine (1.0 equiv), phenylboronic acid (1.2 equiv), K_3PO_4 (2.5 equiv), and 10:1 dioxane:water (0.20 M) under air at 23 °C. The vial was sealed with a rubber septum and evacuated and backfilled thrice with nitrogen. The vial was evacuated and taken into a glove box together with a PTFE-lined cap, after which $Pd(PPh_3)_4$ (0.025 mmol, 5.0 mol%) was added to the vial. The vial was sealed while still in the glove box with a PTFE-lined cap, removed from the glove box, and placed on a stir plate. The resulting mixture was heated to 100 °C and allowed to stir at that temperature overnight. Upon completion of the reaction as judged by TLC (8:2 hexanes:acetone, UV visualization), the mixture was allowed to cool to 23 °C, taken into a pipette, and passed through a short bed of Celite. The solvent was removed *in vacuo*, and the resulting crude residue was purified by flash column chromatography (8:2 hexanes:acetone) to give the title compound as a yellow solid (33 mg, 95%).



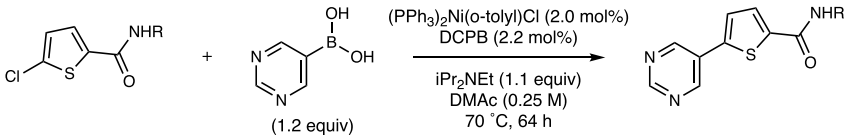
4,5-diphenylpyrimidine (S26). To a 15 mL screw top vial equipped with a stir bar was added 5-bromo-4-phenylpyrimidine (1.0 equiv), phenylboronic acid (1.2 equiv), K_3PO_4 (2.5 equiv), and 10:1 dioxane:water (0.20 M) under air at 23 ˚C. The vial was sealed with a rubber septum and evacuated and backfilled thrice with nitrogen. The vial was evacuated and taken into a glove box together with a PTFE-lined cap, after which $Pd(PPh_3)_4$ (0.025 mmol, 5.0 mol%) was charged into the vial. The vial was sealed while still in the glove box with a PTFE-lined cap, removed from the glove box, and placed on a stir plate. The resulting mixture was heated to 100 ˚C and allowed to stir at that temperature overnight. Upon completion of the reaction as judged by TLC (8:2 hexanes:acetone, UV visualization), the mixture was allowed to cool to 23 ˚C, taken into a pipette and passed through a short bed of Celite. The solvent from the resulting filtrate was removed *in vacuo*, and the resulting crude residue was purified by flash column chromatography (8:2 hexanes:acetone) to give the title compound as a yellow solid (32 mg, 94%).



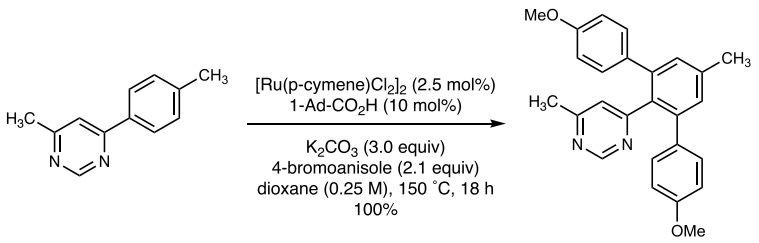
5-bromo-4-phenylpyrimidine (S28). Prepared according to a previously reported protocol.[3] To a 15 mL screw top vial equipped with a stir bar was added 4-phenylpyrimidine (500 mg, 3.2 mmol, 1.0 equiv), sulfuric acid (5.0 mL, 3.2 mmol, 1.0 equiv), HBr (0.75 mL, 5.9 mmol, 1.8 equiv), and $NaNO_2$ (663 mg, 9.6 mmol, 3.0 equiv) under air at 23 ˚C. The resulting mixture was allowed to stir for 15 min at 23 ˚C before the remainder of the HBr (2.3 mL, 17.6 mmol, 5.5 equiv) was added. The vial was sealed with a rubber septum and evacuated and backfilled thrice with nitrogen. The resulting mixture was heated to 60 ˚C and allowed to stir at that temperature for 16 h, at which point the reaction was deemed complete by TLC (20% acetone:hexanes). To the resulting mixture was added water (5 mL) and saturated aqueous $NaHCO_3$ (20 mL) sequentially at 23 ˚C under air. The resulting mixture was allowed to stir vigorously for 20 min at 23 ˚C before $CHCl_3$ (50 mL) was added. The organic phase was separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and the crude residue purified by flash column chromatography (20% acetone:hexanes) to give the desired product as an off white solid (435 mg, 57 %).



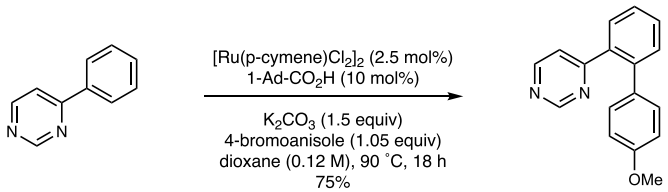
4-methyl-6-phenylpyrimidine (S33). To an oven-dried 15 mL screw top vial with PTFE-lined threads was added 2-chloro-4-phenyl pyrimidine (200 mg, 1.0 mmol, 1.0 equiv), phenylboronic acid (1.2 mmol, 1.2 equiv), and $Pd(PPh_3)Cl_2$ (7.1 mg, 0.010 mmol, 1.0 mol%). The vial was capped with a rubber septum and evacuated and backfilled with nitrogen thrice before a 2 M aqueous solution of Na_2CO_3 (2.5 mL, 5.0 equiv) and 1,4-dioxane (2.5 mL) were added at 23 ˚C. The rubber septum was replaced with a PTFE-lined cap against a nitrogen backflow. The resulting mixture was brought to 90 ˚C and allowed to stir at that temperature for 18 h. The resulting mixture was allowed to cool to 23 ˚C, passed through a short plug of Celite, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (9:1 hexanes:acetone) to give the title compound (126 mg, 76%).



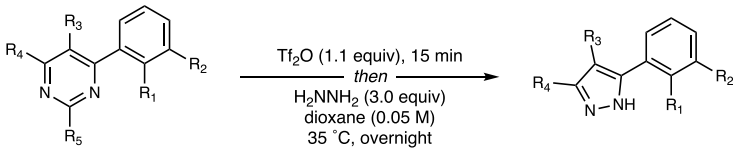
5-(2,4-dimethoxypyrimidin-5-yl)-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)thiophene-2-carboxamide (42). Prepared according to a previously reported protocol.[4] To a flame-dried 20 mL vial under nitrogen atmosphere was added Rivaroxaban® (5-chloro-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)thiophene-2-carboxamide) (436 mg, 1.00 mmol, 1.0 equiv) and (pyrimidin-5-yl)boronic acid (149 mg, 1.20 mmol, 1.2 equiv) at 23 ˚C. The resulting mixture of solids was stirred under vacuum for 1 h at 23 ˚C, after which the vial was filled with anhydrous nitrogen and 1:3 (v:v) DMAc:H_2O (9,73 mL, 0.90 M), and diisopropylethylamine (171 μL, 1.10 mmol, 1.1 equiv) were added at 23 ˚C. The resulting mixture was sparged with anhydrous nitrogen for 1 h. The vial was sealed with a PTFE-lined cap and transferred into a glove box. The vial cap was removed and a 0.083 M stock solution of Ni(DCBP)(*o*-tolyl)Cl in anhydrous acetonitrile(1.33 mL, 0.020 mmol, 2.0 mol%) was added. The vial was sealed with a PTFE-lined cap inside the glove box and the joint was wrapped with PTFE tape and electrical tape. The vial was placed onto a stir plate inside the glove box, and the resulting mixture was allowed to stir for 64 h at 70 ˚C. The resulting mixture was allowed to cool to 23 ˚C and stir at that temperature for 20 min. The vial was removed from the glove box, and the solids were collected by vacuum filtration. The solids were resuspended in 1:3:3 (v:v:v) H_2O:DMAc:DCE (14 mL) in a 20 mL vial, and the resulting mixture was heated to 50 ˚C and allowed to stir at that temperature for 20 min. The mixture was allowed to cool to room temperature, and the solids were collected by vacuum filtration, washed with heptanes, and dried under vacuum at 40 ˚C for 4 h to give the title compound as a white solid (207 mg, 43%).



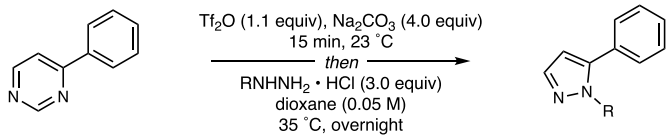
4-(4,4''-dimethoxy-5'-methyl-[1,1':3',1''-terphenyl]-2'-yl)-6-methylpyrimidine (45). Prepared according to a previously reported protocol.[5] To an oven-dried 20 mL sealable pressure tube was added 4-methyl-6-(*p*-tolyl)pyrimidine (**44**) pyrimidine (92 mg, 0.50 mmol, 1.0 equiv), [Ru(p-cymene)Cl_2]$_2$ (7.7 mg, 0.0125 mmol, 2.5 mol%), adamantane-1-carboxylic acid (9.1 mg, 0.05 mmol, 10 mol%), potassium carbonate (207 mg, 1.50 mmol, 3.0 equiv), and 4-bromoanisole (197 mg, 1.05 mmol, 2.1 equiv). The vial was capped with a PTFE septum and evacuated and backfilled with nitrogen thrice before 1,4-dioxane (2.0 mL, 0.25 M) were added at 23 ˚C. The resulting mixture was brought to 150 ˚C and allowed to stir at that temperature for 18 h. The resulting mixture was allowed to cool to 23 ˚C, passed through a short plug of Celite, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (9:1 hexanes:acetone) to give the title compound (149 mg, 75%).



4-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyrimidine. Prepared according to a previously reported protocol.[5] To an oven-dried 20 mL sealable pressure tube was added 4-phenylpyrimidine (156 mg, 1.00 mmol, 1.0 equiv), $[Ru(p\text{-cymene})Cl_2]_2$ (15 mg, 0.025 mmol, 2.5 mol%), adamantane-1-carboxylic acid (18 mg, 0.05 mmol, 10 mol%), potassium carbonate (100 mg, 1.50 mmol, 1.50 equiv), and 4-bromoanisole (100 mg, 1.05 mmol, 1.05 equiv). The vial was capped with a PTFE septum and evacuated and backfilled with nitrogen thrice before 1,4-dioxane (4.2 mL, 0.12 M) were added at 23 ˚C. The resulting mixture was brought to 90 ˚C and allowed to stir at that temperature for 18 h. The resulting mixture was allowed to cool to 23 ˚C, passed through a short plug of Celite, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (9:1 hexanes:acetone) to give the title compound (197 mg, 75%).

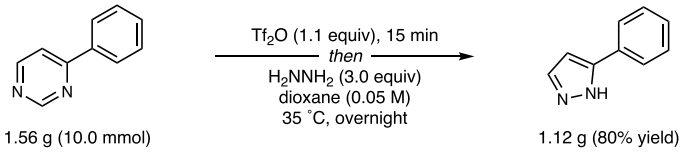


***General Procedure D* for the hydrazine-mediated contraction of 4-arylpyrimidines.** To an oven-dried 1 dram vial was added pyrimidine substrate (0.10 mmol, 1.0 equiv) at 23 ˚C. The vial was evacuated and backfilled with nitrogen thrice before anhydrous 1,4-dioxane (1.30 mL, 0.05 M) was added at 23 ˚C. The vial was sealed with a PTFE-lined cap and transferred into a glove box, after which trifluoromethylsulfonic anhydride (19 μL, 0.11 mmol, 1.1 equiv) was added in the glove box under nitrogen atmosphere. The vials were sealed in the glove box, removed, affixed with a rubber septum, and placed under a positive pressure of nitrogen. The resulting mixtures were allowed to stir under nitrogen at 23 ˚C for 15 min, at which point anhydrous hydrazine (9 μL, 0.30 mmol, 3.0 equiv) was added at 23 ˚C. The vials were then sealed with a PTFE-lined cap and the resulting mixtures were then warmed to 35 ˚C and allowed to stir at that temperature overnight under nitrogen atmosphere. The mixtures were allowed to cool to 23 ˚C, diluted with ethyl acetate (10 mL), passed through a 1-inch plug of silica in a large glass pipette, concentrated *in vacuo*, and the resulting crude residues were purified by preparative TLC (hexanes:acetone) to give the desired 5-arylpyrazole products.



***General Procedure E* for the hydrazine hydrochloride salt-mediated contraction of 4-arylpyrimidines.** An oven-dried 1 dram vial was charged with 4-phenylpyrimidine (15.6 mg, 0.10 mmol, 1.0 equiv) and Na_2CO_3 (43 mg, 0.40 mmol, 4.0 equiv) at 23 °C. The vial was evacuated and backfilled with nitrogen thrice before anhydrous 1,4-dioxane (1.30 mL, 0.05 M) was added at 23 °C. The vial was sealed with a PTFE-lined cap and transferred into a glove box, after which trifluoromethylsulfonic anhydride (19 μL, 0.11 mmol, 1.1 equiv) was added in the glove box under nitrogen atmosphere. The resulting mixture was allowed to stir in the glove box at 23 °C for 15 min. To the resulting mixture was added hydrazine hydrochloride salt or a derivative thereof (0.30 mmol, 3.0 equiv) at 23 °C. The vial was then sealed with a PTFE-lined cap and the resulting mixture was then warmed to 35 °C and allowed to stir at that temperature overnight under nitrogen atmosphere. The mixture was allowed to cool to 23 °C and diluted with ethyl acetate (50 mL) and water (50 mL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic extracts were washed with 6N aqueous HCl (20 mL) and saturated aqueous $NaHCO_3$ (50 mL). The phases were separated, and the organic phase was dried over anhydrous Na_2SO_4, concentrated *in vacuo*, and the resulting crude residue was purified by flash column chromatography (95:5 hexanes:ethyl acetate) to give the desired product.

2.7. 10.0 mmol Contraction Procedure

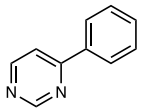


1.56 g (10.0 mmol) 1.12 g (80% yield)

To a flame-dried 250 mL round-bottomed flask sealed with a rubber septum under nitrogen atmosphere in a glove box was added tifluoromethanesulfonic anhydride (1.9 mL, 11.0 mmol, 1.1 equiv). The flask was removed from the glove box. A nitrogen inlet was affixed to the flask, and anhydrous 1,4-dioxane (1.30 mL, 0.05 M) was added at 23 ˚C. 4-Phenylpyrimidine (1.56 g, 10.0 mmol, 1.0 equiv) was charged in one portion against a positive pressure of nitrogen at 23 ˚C. The resulting mixture was allowed to stir under nitrogen at 23 ˚C for 1 h, after which the mixture was heated to 35 ˚C and allowed to stir at that temperature for 1 h before anhydrous hydrazine (0.94 mL, 30 mmol, 3.0 equiv) was added dropwise. The resulting mixture was allowed to stir overnight under an atmosphere of nitrogen at 35 ˚C. Reaction progress was monitored by TLC (8:2 hexanes:acetone, RF_{pdt} = 0.18). The resulting mixture was allowed to cool to 23 ˚C and diluted with ethyl acetate (100 mL). The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (100 mL), the organic phase was separated, and the aqueous phase was extracted twice with ethyl acetate (100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 (granules), filtered, and concentrated *in vacuo*. The resulting crude residue as purified by flash column chromatography (6 inches of dry SiO_2 in a 50 mm diameter column, 8:2 hexanes:acetone; product elution occurred between 20 mL fractions 33–60) to afford 5-phenyl-1*H*-pyrazole as a pale amber crystalline solid (1.12 g, 80%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.30 (s, 1H), 7.87 – 7.69 (m, 2H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.38 – 7.28 (m, 1H), 6.62 (d, *J* = 2.3 Hz, 1H).

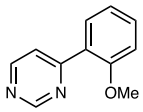
3. Product Characterization



4-phenylpyrimidine (S1). Prepared according to *General Procedure A* from acetophenone to give the title compound (573 mg, 76%).

Physical properties: pale amber crystalline solid
Melting point: 60–62 ˚C
R_f = 0.30 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.30 (s, 1H), 9.00 – 8.63 (m, 1H), 8.23 – 8.00 (m, 2H), 7.74 (d, *J* = 5.2 Hz, 1H), 7.64 – 7.41 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 164.00, 159.05, 157.37, 136.53, 131.16, 129.08, 127.17.

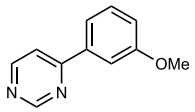
The spectrum matched that which was previously reported in the literature.[6]



4-(2-methoxyphenyl)pyrimidine (S2). Prepared according to *General Procedure A* from *ortho*-methoxy acetophenone to give the title compound (140 mg, 75 %).

Physical properties: yellow solid
R_f = 0.26 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (s, 1H), 8.71 (s, 1H), 8.13 – 7.87 (m, 2H), 7.52 – 7.39 (m, 1H), 7.11 (dd, *J* = 8.0, 6.9 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 4H).

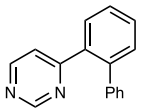
The spectrum matched that which was previously reported in the literature.[6]



4-(3-methoxyphenyl)pyrimidine (S3). Prepared according to *General Procedure A* from *meta*-methoxy acetophenone to give the title compound (131 mg, 70%).

Physical properties: orange solid
R_f = 0.27 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.27 (d, *J* = 1.4 Hz, 1H), 8.77 (d, *J* = 5.4 Hz, 1H), 7.81 – 7.66 (m, 2H), 7.63 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.07 (ddd, *J* = 8.3, 2.7, 0.9 Hz, 1H), 3.91 (s, 3H).

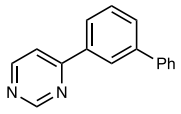
The spectrum matched that which was previously reported in the literature.[6]



4-(2-phenylphenyl)pyrimidine (S4). Prepared according to *General Procedure A* from 1-([1,1'-biphenyl]-2-yl)ethan-1-one to give the title compound (107 mg, 90%).

Physical properties: brick red solid
R_f = 0.35 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, Acetone): δ 9.13 (d, *J* = 1.5 Hz, 1H), 8.47 (d, *J* = 5.2 Hz, 1H), 7.77 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.57 (dtd, *J* = 23.0, 7.5, 1.5 Hz, 2H), 7.48 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.31 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.18 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.97 (dd, *J* = 5.4, 1.5 Hz, 1H).

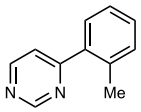
The spectrum matched that which was previously reported in the literature.[7]



4-(2-phenylphenyl)pyrimidine (S5). Prepared from 4-(3-bromophenyl)pyrimidine to give the title compound (33 mg, 95%).

Physical properties: pale amber oil
R_f = 0.37 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, Acetone): δ 9.24 (d, *J* = 1.5 Hz, 1H), 8.85 (d, *J* = 5.3 Hz, 1H), 8.51 (t, *J* = 1.9 Hz, 1H), 8.22 (dt, *J* = 7.9, 1.4 Hz, 1H), 8.12 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.84 (ddd, *J* = 7.7, 1.9, 1.1 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.51 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.46 – 7.36 (m, 1H).
^{13}C NMR (126 MHz, Acetone): δ 205.26, 158.98, 157.93, 129.58, 129.52, 128.96, 127.72, 127.04, 126.01, 125.58, 117.21.

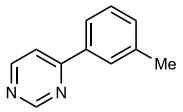
The spectra matched those which were previously reported in the literature.[7]



4-(2-methylphenyl)pyrimidine (S6). Prepared according to *General Procedure A* from *ortho*-methyl acetophenone to give the title compound (120 mg, 63%).

Physical properties: amber oil
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.30 (d, *J* = 1.4 Hz, 1H), 8.79 (d, *J* = 5.2 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 2.44 (s, 3H).

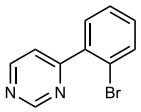
The spectrum matched that which was previously reported in the literature.[6]



4-(3-methylphenyl)pyrimidine (S7). Prepared according to *General Procedure A* from *meta*-methyl acetophenone to give the title compound (69 mg, 54 %).

Physical properties: yellow oil
R_f = 0.32 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.98 – 8.58 (m, 1H), 7.92 (d, *J* = 2.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.76 – 7.64 (m, 1H), 7.39 (td, *J* = 7.7, 2.1 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 2.44 (d, *J* = 2.1 Hz, 3H).

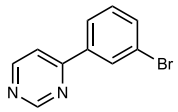
The spectrum matched that which was previously reported in the literature.[6]



4-(2-bromophenyl)pyrimidine (S8). Prepared according to *General Procedure A* from *ortho*-bromo acetophenone to give the title compound (600 mg, 51 %).

Physical properties: off-white crystalline solid
R_f = 0.34 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (d, *J* = 1.5 Hz, 1H), 8.82 (d, *J* = 5.2 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.60 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.45 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33 (td, *J* = 7.7, 1.8 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.32, 158.95, 156.57, 138.60, 133.73, 131.37, 131.25, 131.02, 129.10, 127.87, 127.22, 121.99, 121.33, 30.94.

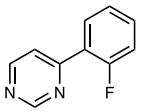
The spectra matched those which were previously reported in the literature.[8]



4-(3-bromophenyl)pyrimidine (S9). Prepared according to *General Procedure A* from *meta*-bromo acetophenone to give the title compound (172 mg, 97%).

Physical properties: off white crystalline solid
R_f = 0.33 (silica gel, 20% acetone/hexanes)
Melting point: 91–92 ˚C
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (d, *J* = 1.4 Hz, 1H), 8.81 (d, *J* = 5.4 Hz, 1H), 8.28 (t, *J* = 1.9 Hz, 1H), 8.02 (ddd, *J* = 7.9, 1.7, 1.0 Hz, 1H), 7.71 (dd, *J* = 5.4, 1.4 Hz, 1H), 7.66 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$):δ 162.57, 159.03, 157.59, 138.48, 134.09, 130.58, 130.32, 125.70, 123.39, 117.09.

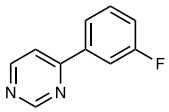
The spectra matched those which were previously reported in the literature.[8]



4-(2-fluorophenyl)pyrimidine (S10). Prepared according to *General Procedure A* from *ortho*-fluoro acetophenone to give the title compound (80 mg, 42 %).

Physical properties: pale yellow solid
R_f = 0.26 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.17 (td, *J* = 7.9, 1.9 Hz, 1H), 7.49 (dddd, *J* = 8.3, 7.1, 5.0, 1.9 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.20 (ddd, *J* = 11.6, 8.3, 1.2 Hz, 1H).

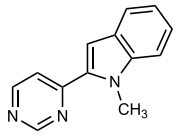
The spectrum matched that which was previously reported in the literature.[9]



4-(3-fluorophenyl)pyrimidine (S11). Prepared according to *General Procedure A* from *meta*-fluoro acetophenone to give the title compound (73 mg, 39%).

Physical properties: off white solid
R_f = 0.29 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.30 (s, 1H), 8.83 (s, 1H), 7.93 – 7.82 (m, 2H), 7.73 (d, *J* = 5.3 Hz, 1H), 7.51 (td, *J* = 8.2, 5.9 Hz, 1H), 7.23 (td, *J* = 8.4, 2.5 Hz, 1H).

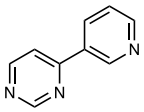
The spectrum matched that which was previously reported in the literature.[9]



1-methyl-3-(pyrimidin-4-yl)-1*H*-indole (S12). Prepared according to *General Procedure A* from 1-(1-methyl-1*H*-indol-3-yl)ethan-1-one to give the title compound (57 mg, 24%).

Physical properties: dark amber oil
R_f = 0.59 (silica gel, 50% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (d, *J* = 1.4 Hz, 1H), 8.61 (d, *J* = 5.5 Hz, 1H), 8.44 – 8.29 (m, 1H), 7.90 (s, 1H), 7.61 (dd, *J* = 5.4, 1.4 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.33 (pd, *J* = 7.1, 1.4 Hz, 2H), 3.89 (s, 3H).

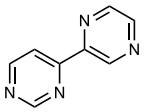
The spectrum matched that which was previously reported in the literature.[10]



4-(pyridin-3-yl)pyrimidine (S13). Prepared according to *General Procedure A* from 1-(pyridin-3-yl)ethan-1-one to give the title compound (183 mg, 71%).

Physical properties: dark orange oil
R_f = 0.51 (silica gel, 50% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 – 9.23 (m, 2H), 8.84 (d, *J* = 5.3 Hz, 1H), 8.76 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.44 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.77 (dd, *J* = 5.3, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.0, 4.9, 1.0 Hz, 1H).

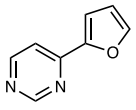
The spectrum matched that which was previously reported in the literature.[11]



4-(pyrazin-2-yl)pyrimidine (S14). Prepared according to *General Procedure A* from 1-(pyrazin-2-yl)ethan-1-one to give the title compound (25 mg, 11%).

Physical properties: pale yellow solid
R_f = 0.20 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (s, 1H), 9.35 (s, 1H), 8.92 (d, *J* = 5.2 Hz, 1H), 8.74 – 8.67 (m, 2H), 8.35 (d, *J* = 5.2 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.75, 158.18, 146.40, 144.06, 143.74, 117.78.
HRMS (ESI): calculated for $C_8H_7N_4^+$ [M + H^+] 159.0665; found 159.0747.

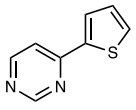
The spectra matched those which were previously reported in the literature.[12]



4-(furan-2-yl)pyrimidine (S15). Prepared according to *General Procedure A* from 1-(furan-2-yl)ethan-1-one to give the title compound (53 mg, 24%).

Physical properties: off-white solid
R_f = 0.27 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (d, *J* = 1.5 Hz, 1H), 8.72 (d, *J* = 5.5 Hz, 1H), 7.62 (dd, *J* = 5.4, 1.5 Hz, 2H), 7.32 (d, *J* = 3.5 Hz, 1H), 6.60 (dd, *J* = 3.6, 1.7 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.76, 157.19, 155.34, 151.43, 145.49, 114.84, 112.91,

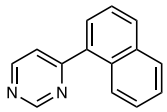
The spectrum matched that which was previously reported in the literature.[8]



4-(thiophen-2-yl)pyrimidine (S16). Prepared according to *General Procedure A* from 1-(thiophen-2-yl)ethan-1-one to give the title compound (148 mg, 58%).

Physical properties: pale orange solid
R_f = 0.17 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.14 (d, *J* = 1.4 Hz, 1H), 8.69 (d, *J* = 5.4 Hz, 1H), 7.79 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.57 (ddd, *J* = 11.9, 5.2, 1.3 Hz, 2H), 7.18 (dd, *J* = 5.0, 3.8 Hz, 1H).

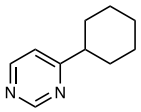
The spectrum matched that which was previously reported in the literature.[8]



4-(naphthalen-2-yl)pyrimidine (S17). Prepared according to *General Procedure A* from 1-(naphthalen-1-yl)ethan-1-one to give the title compound (207 mg, 85%).

Physical properties: off-white solid
R_f = 0.16 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (d, *J* = 1.4 Hz, 1H), 8.87 (d, *J* = 5.2 Hz, 1H), 8.25 – 8.12 (m, 1H), 7.99 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.72 – 7.62 (m, 2H), 7.62 – 7.50 (m, 3H).

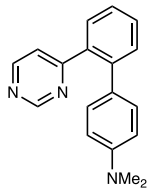
The spectrum matched that which was previously reported in the literature.[13]



4-cyclohexylpyrimidine (S18). Prepared according to *General Procedure A* from 1-cyclohexyl ethanone to give the title compound (71 mg, 37%).

Physical properties: yellow oil
R_f = 0.27 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, *J* = 1.5 Hz, 1H), 8.61 (d, *J* = 5.3 Hz, 1H), 7.17 (dd, *J* = 5.3, 1.4 Hz, 1H), 2.65 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.95 (ddt, *J* = 12.3, 3.6, 1.8 Hz, 2H), 1.86 (ddd, *J* = 9.6, 5.0, 2.0 Hz, 2H), 1.76 (dtt, *J* = 12.6, 3.2, 1.5 Hz, 1H), 1.57 – 1.27 (m, 5H).

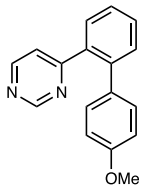
The spectrum matched that which was previously reported in the literature.[1]



***N*,*N*-dimethyl-2'-(pyrimidin-4-yl)-[1,1'-biphenyl]-4-amine (S19).** Prepared according to *General Procedure A* from 2'-(*para*-dimethylaminophenyl)-acetophenone to give the title compound (64 mg, 56%).

Physical properties: yellow solid
R_f = 0.31 (silica gel, 5% methanol/dichloromethane)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26 (d, *J* = 1.4 Hz, 1H), 8.40 (d, *J* = 5.4 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.38 (m, 3H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.89 (dd, *J* = 5.3, 1.4 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 2.96 (s, 6H).

The spectrum matched that which was previously reported in the literature.[7]

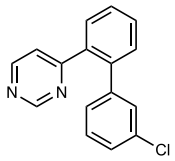


4-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyrimidine (S20). Prepared according to *General Procedure A* from 2'-(*para*-methoxyphenyl)-acetophenone to give the title compound (35 mg, 42%).

Physical properties: yellow solid
R_f = 0.32 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.73 – 8.01 (m, 1H), 7.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 – 7.41 (m, 3H), 7.17 – 7.02 (m, 2H), 6.93 – 6.85 (m, 1H), 6.85 – 6.80 (m, 1H), 3.81 (s, 3H).

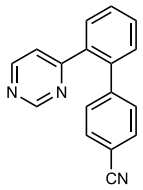
The spectrum matched that which was previously reported in the literature.[7]

This compound was also prepared according to a modified version of a previously reported protocol to give the title compound (197 mg, 75%);[5] the procedure for the synthesis of **45** or **44** was employed with 1.05 equiv of 4-bromoanisole and 1.50 equiv of potassium carbonate at 90 ˚C in 1,4-dioxane (0.12 M).



4-(3'-chloro-[1,1'-biphenyl]-2-yl)pyrimidine (S21). Prepared according to *General Procedure A* from 2'-(*meta*-chlorophenyl)-acetophenone to give the title compound (90 mg, 63%).

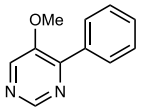
Physical properties: pale yellow solid
R_f = 0.37 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 1.4 Hz, 1H), 8.46 (d, *J* = 5.2 Hz, 1H), 7.82 – 7.72 (m, 1H), 7.59 – 7.49 (m, 2H), 7.49 – 7.39 (m, 1H), 7.18 (td, *J* = 7.7, 0.7 Hz, 1H), 6.97 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.90 (dd, *J* = 5.3, 1.4 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.26, 159.16, 155.96, 142.53, 139.75, 136.90, 134.54, 130.87, 130.64, 130.21, 129.72, 129.56, 128.59, 128.11, 127.63, 122.40.
HRMS (ESI): calculated for $C_{16}H_{12}ClN_2^+$ [M + H^+] 267.0684; found 267.0686.



4-(4'-cyano-[1,1'-biphenyl]-2-yl)pyrimidine (S22). Prepared according to *General Procedure A* from 2'-(*meta*-nitrophenyl)-acetophenone to give the title compound (54 mg, 37%).

Physical properties: bright purple solid
R_f = 0.34 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.5 Hz, 1H), 8.53 (d, *J* = 5.3 Hz, 1H), 7.84 – 7.74 (m, 1H), 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.08 (dd, *J* = 5.2, 1.4 Hz, 1H).

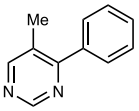
The spectrum matched that which was previously reported in the literature.[5]



5-methoxy-4-phenylpyrimidine (S23). Prepared according to *General Procedure A* from 2-methoxy acetophenone to give the title compound (87 mg, 47%).

Physical properties: amber solid
R_f = 0.28 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (s, 1H), 8.46 (s, 1H), 8.23 – 7.91 (m, 2H), 7.48 (dd, *J* = 5.2, 1.9 Hz, 3H), 3.99 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 153.89, 151.36, 151.25, 140.44, 135.15, 130.14, 129.56, 128.26, 56.12.

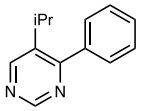
The spectra matched those which were previously reported in the literature.[1]



5-methyl-4-phenylpyrimidine (S24). Prepared according to *General Procedure A* from 2-methyl acetophenone to give the title compound (172 mg, 90%).

Physical properties: orange solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.12 (s, 1H), 8.62 (s, 1H), 7.62 (d, *J* = 6.7 Hz, 2H), 7.58 – 7.40 (m, 3H), 2.40 (d, *J* = 2.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.03, 158.74, 156.64, 137.89, 129.44, 128.84, 128.47, 128.21, 17.16.

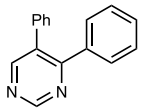
The spectra matched those which were previously reported in the literature.[1]



5-isopropyl-4-phenylpyrimidine (S25). Prepared according to *General Procedure A* from 2-isopropyl acetophenone to give the title compound (29 mg, 17%).

Physical properties: amber oil
R_f = 0.36 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.77 (s, 1H), 7.54 – 7.44 (m, 5H), 3.22 (hept, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H).

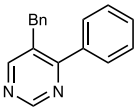
The spectrum matched that which was previously reported in the literature.[1]



4,5-diphenylpyrimidine (S26). Prepared from 5-bromo-4-phenylpyrimidine to give the title compound (33 mg, 94%).

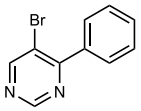
Physical properties: off white solid
R_f = 0.39 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, Acetone): δ 9.20 (s, 1H), 8.76 (s, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.35 (m, 4H), 7.33 – 7.27 (m, 4H).
^{13}C NMR (126 MHz, Acetone): δ 163.03, 158.19, 157.39, 137.82, 136.56, 133.19, 129.80, 129.40, 129.24, 128.69, 127.98, 127.96.

The spectra matched those which were previously reported in the literature.[14]



5-benzyl-4-phenylpyrimidine (S27). Prepared according to *General Procedure A* from 2-benzyl acetophenone to give the title compound (69 mg, 39%).

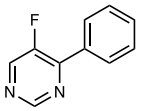
Physical properties: yellow solid
R_f = 0.43 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.61 (s, 1H), 7.80 – 7.36 (m, 5H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.22 (dd, *J* = 8.3, 6.0 Hz, 1H), 7.07 – 6.95 (m, 2H), 4.09 (s, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.80, 159.23, 156.90, 139.06, 137.78, 129.59, 128.93, 128.89, 128.79, 128.65, 126.84, 36.11.
HRMS (ESI): calculated for $C_{17}H_{15}N_2^+$ [M + H^+] 247.1230; found 247.1230.



5-bromo-4-phenylpyrimidine (S28). Prepared from 4-phenylpyrimidine to give the title compound (432 mg, 57%).

Physical properties: flaky off white solid
R_f = 0.35 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (s, 1H), 8.93 (s, 1H), 7.92 – 7.68 (m, 2H), 7.51 (dd, *J* = 5.0, 2.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 164.35, 160.15, 156.91, 136.78, 130.35, 129.28, 128.31.

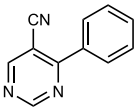
The spectra matched those which were previously reported in the literature.[3]



5-fluoro-4-phenylpyrimidine (S29). Prepared according to *General Procedure A* from 2-fluoro acetophenone to give the title compound (34 mg, 18%).

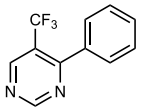
Physical properties: yellow oil
R_f = 0.32 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.08 (d, *J* = 3.1 Hz, 1H), 8.64 (d, *J* = 3.5 Hz, 1H), 8.23 – 8.07 (m, 2H), 7.60 – 7.47 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.88, 154.74, 154.60, 154.54, 151.98, 151.92, 146.10, 145.91, 141.27, 132.84, 132.80, 131.26, 129.17, 129.12, 128.83, 126.81, 30.94.

The spectra matched those which were previously reported in the literature.[15]



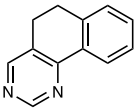
5-cyano-4-phenylpyrimidine (S30). Prepared according to *General Procedure A* from 2-cyano acetophenone to give the title compound as a bright yellow solid (94 mg, 50%).

Physical properties: red solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 9.06 (s, 1H), 8.31 – 7.90 (m, 2H), 7.71 – 7.53 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.91, 161.85, 160.17, 134.66, 132.32, 129.14, 129.02, 115.71, 106.41.
HRMS (ESI): calculated for $C_{11}H_8N_3^+$ [M + H^+] 182.0713; found 182.0672.



5-trifluoromethyl-4-phenylpyrimidine (S31). Prepared according to *General Procedure A* from 2-trifluoromethyl acetophenone to give the title compound as a bright yellow solid (94 mg, 50%).

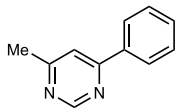
Physical properties: pale yellow solid
R_f = 0.33 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 9.07 (s, 1H), 8.29 – 7.97 (m, 2H), 7.69 – 7.52 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.05, 161.99, 160.30, 134.80, 132.46, 129.27, 129.16, 115.85, 106.55.
HRMS (ESI): calculated for $C_{11}H_8F_3N_2^+$ [M + H^+] 225.0634; found xx.



5,6-dihydrobenzo[*h*]quinazoline (S32). Prepared according to *General Procedure A* from tetralone to give the title compound as a dark orange solid (160 mg, 64%).

Physical properties: pale amber solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.55 (s, 1H), 8.34 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.46 – 7.36 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 3.03 – 2.91 (m, 4H).

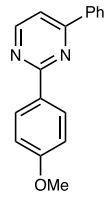
The spectra matched those which were previously reported in the literature.[1]



4-methyl-6-phenylpyrimidine (S33). Prepared 4-chloro-6-methylpyrimidine to give the title compound (126 mg, 73%).

Physical properties: pale yellow oil
R_f = 0.35 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.15 (d, *J* = 2.3 Hz, 1H), 8.29 – 7.90 (m, 2H), 7.59 (s, 1H), 7.51 (dt, *J* = 5.0, 1.8 Hz, 3H), 2.75 – 2.44 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.49, 163.82, 158.73, 136.81, 130.86, 128.99, 127.14, 116.51, 24.41.

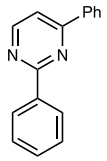
The spectra matched those which were previously reported in the literature.[16]



2-(4-methoxyphenyl)-4-phenylpyrimidine (S34). Prepared according to *General Procedure C* from 2-chloro-4-phenyl pyrimidine and (*para*-methoxy)phenylboronic acid to give the title compound (270 mg, 99%).

Physical properties: white solid
R_f = 0.26 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$)L δ 8.79 (d, *J* = 5.3 Hz, 1H), 8.59 – 8.51 (m, 2H), 8.26 – 8.17 (m, 2H), 7.54 (dq, *J* = 5.2, 1.9 Hz, 4H), 7.07 – 6.99 (m, 2H), 3.90 (s, 3H).

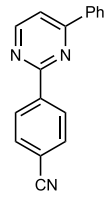
The spectrum matched that which was previously reported in the literature.[17]



2,4-diphenylpyrimidine (S35). Prepared according to *General Procedure C* from 2-chloro-4-phenyl pyrimidine and phenylboronic acid to give the title compound (219 mg, 94%).

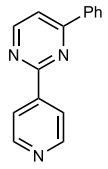
Physical properties: white solid
R_f = 0.35 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 5.3 Hz, 1H), 8.58 (dt, *J* = 7.1, 2.5 Hz, 2H), 8.24 (q, *J* = 3.5, 3.0 Hz, 2H), 7.62 (d, *J* = 5.3 Hz, 1H), 7.59 – 7.47 (m, 6H).

The spectrum matched that which was previously reported in the literature.[18]



2-(4-cyanophenyl)-4-phenylpyrimidine (S36). Prepared according to *General Procedure C* from 2-chloro-4-phenyl pyrimidine and (*para*-cyano)phenylboronic acid to give the title compound (104 mg, 40%).

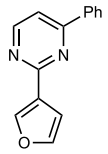
Physical properties: white solid
R_f = 0.20 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (d, *J* = 5.2 Hz, 1H), 8.74 – 8.65 (m, 2H), 8.28 – 8.15 (m, 2H), 7.86 – 7.80 (m, 2H), 7.69 (d, *J* = 5.3 Hz, 1H), 7.59 – 7.53 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.19, 132.51, 131.50, 129.24, 128.94, 127.39, 115.63, 114.15.
HRMS (ESI): calculated for $C_{17}H_{12}N_3^+$ [M + H^+] 258.1026; found 258.1029.



4-phenyl-2-(pyridin-4-yl)pyrimidine (S37). Prepared according to *General Procedure C* from 2-chloro-4-phenyl pyrimidine and pyridin-4-yl boronic acid to give the title compound (45 mg, 19%).

Physical properties: yellow solid
R_f = 0.25 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, *J* = 5.2 Hz, 1H), 8.86 – 8.76 (m, 2H), 8.48 – 8.38 (m, 2H), 8.29 – 8.18 (m, 2H), 7.72 (d, *J* = 5.3 Hz, 1H), 7.56 (ddt, *J* = 5.7, 3.9, 2.2 Hz, 3H).

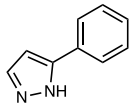
The spectrum matched that which was previously reported in the literature.[19]



2-(furan-3-yl)-4-phenylpyrimidine (S38). Prepared according to *General Procedure C* from 2-chloro-4-phenyl pyrimidine and furan-3-yl boronic acid to give the title compound (221 mg, 99%).

Physical properties: white solid
R_f = 0.20 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.74 (d, *J* = 5.3 Hz, 1H), 8.34 (dd, *J* = 1.7, 0.8 Hz, 1H), 8.21 – 8.12 (m, 2H), 7.58 – 7.47 (m, 5H), 7.16 (dd, *J* = 1.8, 0.8 Hz, 1H).

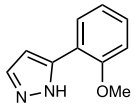
The spectrum matched that which was previously reported in the literature.[20]



5-phenyl-1*H*-pyrazole (1). Prepared according to *General Procedure D* from 4-phenylpyrimidine to give the title compound (13.0 mg, 90%).

Physical properties: yellow crystalline solid
Melting point: 159–160 ˚C
R_f = 0.16 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.39 – 7.29 (m, 1H), 6.64 (s, 1H).

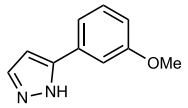
The spectrum matched that which was previously reported in the literature.[21]



5-(2-methoxyphenyl)-1*H*-pyrazole (2a). Prepared according to *General Procedure D* from 4-(*ortho*-methoxyphenyl)pyrimidine to give the title compound (12.2 mg, 70 %).

Physical properties: yellow oil
R_f = 0.13 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 – 7.78 (s, 1H), 7.69 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.33 (ddd, *J* = 8.7, 7.5, 1.7 Hz, 1H), 7.08 – 7.01 (m, 2H), 6.68 (s, 1H), 4.01 (s, 3H).

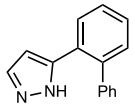
The spectrum matched that which was previously reported in the literature.[22]



5-(3-methoxyphenyl)-1*H*-pyrazole (2b). Prepared according to *General Procedure D* from 4-(*meta*-methoxyphenyl)pyrimidine to give the title compound (11 mg, 63 %).

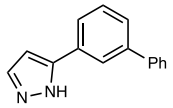
Physical properties: yellow oil
R_f = 0.13 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.73 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.33 (s, 1H), 7.32 – 7.28 (m, 1H), 3.86 (s, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.14, 134.57, 130.98, 128.63, 127.53, 125.83, 118.46, 59.14.

The spectra matched those which were previously reported in the literature.[21]



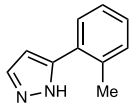
5-([1,1'-biphenyl]-2-yl)-1*H*-pyrazole (3a). Prepared according to *General Procedure D* from 4-(*meta*-phenylphenyl)pyrimidine to give the title compound (19.5 mg, 89 %).

Physical properties: white solid
R_f = 0.25 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.24 (d, *J* = 1.5 Hz, 1H), 8.38 (d, *J* = 5.2 Hz, 1H), 7.78 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.46 (dd, *J* = 7.1, 1.9 Hz, 1H), 7.28 (q, *J* = 2.8 Hz, 3H), 7.23 – 7.10 (m, 2H), 6.83 (dd, *J* = 5.3, 1.4 Hz, 1H).
13C
HRMS (ESI): calculated for $C_{15}H_{13}N_2^+$ [M + H^+] 221.1073; found 221.1075.



5-([1,1'-biphenyl]-3-yl)-1*H*-pyrazole (3b). Prepared according to *General Procedure D* from 4-(*meta*-phenylphenyl)pyrimidine to give the title compound (16.8 mg, 76%).

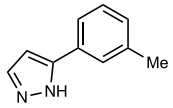
Physical properties: yellow oil
R_f = 0.27 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (t, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.59 – 7.53 (m, 1H), 7.47 (dt, *J* = 12.5, 7.5 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 2.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.28, 141.87, 140.89, 133.20, 132.49, 129.28, 128.82, 127.51, 127.22, 126.98, 124.68, 124.66, 102.96, 66.38, 54.96, 30.96, 1.04.
HRMS (ESI): calculated for $C_{15}H_{13}N_2^+$ [M + H^+] 221.1073; found 221.1075.



5-(2-methylphenyl)-1*H*-pyrazole (4a). Prepared according to *General Procedure D* from 4-(*ortho*-methylphenyl)pyrimidine to give the title compound (12 mg, 76 %).

Physical properties: yellow solid
R_f = 0.14 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.53 (d, *J* = 2.2 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.12 (m, 3H), 6.44 – 6.28 (m, 1H), 2.35 (s, 3H).

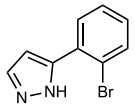
The spectrum matched that which was previously reported in the literature.[23]



5-(3-methylphenyl)-1*H*-pyrazole (4b). Prepared according to *General Procedure D* from 4-(*meta*-methylphenyl)pyrimidine to give the title compound (11.5 mg, 73%).

Physical properties: white solid
R_f = 0.14 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, CDCl3) δ 7.61 (d, *J* = 2.2 Hz, 1H), 7.56 (d, *J* = 1.9 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 2.39 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.93, 138.52, 133.66, 131.70, 128.96, 128.76, 126.46, 122.89, 102.76, 66.38, 54.96, 21.46.

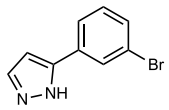
The spectra matched those which were previously reported in the literature.[22]



5-(2-bromophenyl)-1*H*-pyrazole (5a). Prepared according to *General Procedure D* from 4-(*ortho*-bromophenyl)pyrimidine to give the title compound (9 mg, 40 %).

Physical properties: pale yellow solid
R_f = 0.17 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, CDCl3): δ 7.70 – 7.56 (m, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.21 – 7.12 (m, 2H), 6.93 – 6.83 (m, 2H), 6.10 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H).

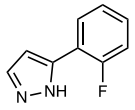
The spectrum matched that which was previously reported in the literature.[21]



5-(3-bromophenyl)-1*H*-pyrazole (5b). Prepared according to *General Procedure D* from 4-(*meta*-bromophenyl)pyrimidine to give the title compound as a pale yellow solid (18.2 mg, 82 %).

Physical properties: pale yellow solid
R_f = 0.19 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, Acetone): δ 12.31 (s, 1H), 8.06 (dt, *J* = 5.9, 1.9 Hz, 1H), 7.86 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.78 (d, *J* = 2.3 Hz, 1H), 7.47 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H).

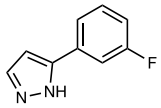
The spectrum matched that which was previously reported in the literature.[24]



5-(2-fluorophenyl)-1*H*-pyrazole (6a). Prepared according to *General Procedure D* from 4-(*ortho*-fluorophenyl)pyrimidine to give the title compound (8.9 mg, 55 %).

Physical properties: dark yellow solid
R_f = 0.14 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 2H), 7.63 (d, *J* = 2.2 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.39 – 7.29 (m, 1H), 6.64 (s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.17, 162.21, 149.13, 134.58, 134.52, 132.13, 130.40, 130.33, 121.42, 121.40, 118.12, 114.99, 114.82, 112.80, 112.62, 103.10, 67.35, 24.93, 17.99.

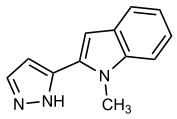
The spectrum matched that which was previously reported in the literature.[23]



5-(3-fluorophenyl)-1*H*-pyrazole (6b). Prepared according to *General Procedure D* from 4-(*meta*-fluorophenyl)pyrimidine to give the title compound (7.7 mg, 47%).

Physical properties: dark yellow crystalline solid
R_f = 0.12 (silica gel, 20% acetone/hexanes)
Melting point: 62–64 ˚C
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.3 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.38 (td, *J* = 8.0, 6.0 Hz, 1H), 7.03 (td, *J* = 8.3, 2.5 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H).

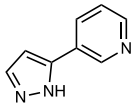
The spectrum matched that which was previously reported in the literature.[22]



1-methyl-3-(1*H*-pyrazol-5-yl)-1*H*-indole (7). Prepared according to *General Procedure A* from 1-methyl-3-(pyrimidin-4-yl)-1*H*-indole to give the title compound (17 mg, 81%).

Physical properties: yellow oil
R_f = 0.18 (silica gel, 50% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.29 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.21 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 3.75 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.31, 126.89, 126.00, 122.38, 120.37, 109.65, 107.27, 102.72, 33.00, 31.08, 29.84, 29.67, 29.42, 14.27.
HRMS (ESI): calculated for $C_{12}H_{12}N_3^+$ [M + H^+] 198.1026; found 198.1024.

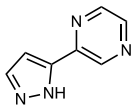
The spectra matched those which were previously reported in the literature.[25]



3-(1*H*-pyrazol-5-yl)pyridine (8a). Prepared according to *General Procedure A* from 4-(pyridin-3-yl)pyrimidine to give the title compound (6.7 mg, 46%).

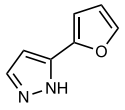
Physical properties: orange oil
R_f = 0.13 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (d, *J* = 2.2 Hz, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 8.15 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.0, 4.9 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H).

The spectrum matched that which was previously reported in the literature.[26]



2-(1*H*-pyrazol-5-yl)pyrazine (8b). Prepared according to *General Procedure A* from 4-(pyrazin-2-yl)pyrimidine to give the title compound (3.5 mg, 24%)

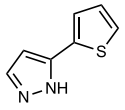
Physical properties: dark amber oil
R_f = 0.12 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (d, *J* = 1.7 Hz, 1H), 8.57 (t, *J* = 2.0 Hz, 1H), 8.51 (d, *J* = 2.6 Hz, 1H), 7.70 (d, *J* = 2.2 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H).
13C NMR
HRMS (ESI): calculated for $C_7H_7N_4^+$ [M + H^+] 147.0665; found 147.0665.



5-(furan-2-yl)-1*H*-pyrazole (9). Prepared according to *General Procedure A* from 4-(furan-2-yl)pyrimidine to give the title compound (11 mg, 56%).

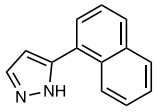
Physical properties: white solid
R_f = 0.16 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.46 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.54 (d, *J* = 2.2 Hz, 1H), 6.51 – 6.44 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 147.52, 142.21, 111.57, 106.45, 102.42.

The spectra matched those which were previously reported in the literature.[27]



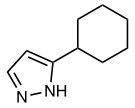
5-(thiophen-2-yl)-1*H*-pyrazole (10). Prepared according to *General Procedure A* from 1-(thiophen-2-yl)ethan-1-one to give the title compound (13 mg, 87%)

Physical properties: white solid
R_f = 0.19 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.34 (dd, *J* = 3.5, 1.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.54 (d, *J* = 2.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 145.67, 135.74, 131.69, 127.72, 124.87, 124.24, 102.89, 77.36, 66.47.
HRMS (ESI): calculated for $C_7H_7N_2S^+$ [M + H^+] 151.0324; found 151.0324.



5-(naphthalen-2-yl)-1*H*-pyrazole (11). Prepared according to *General Procedure A* from 4-(naphthalen-1-yl)pyrimidine to give the title compound (14.5 mg, 77%).

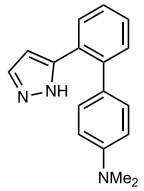
Physical properties: white crystalline solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 – 8.14 (m, 1H), 8.03 – 7.78 (m, 2H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.59 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.56 – 7.41 (m, 3H), 6.60 (d, *J* = 2.1 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 146.97, 134.05, 133.85, 131.39, 129.65, 128.91, 128.43, 127.18, 126.62, 126.09, 125.53, 125.30, 120.70, 118.16, 106.50, 66.33, 30.95, 24.96, 17.96.
HRMS (ESI): calculated for $C_{13}H_{11}N_2^+$ [M + H^+] 195.0917; found 195.0916.



5-cyclohexyl-1*H*-pyrazole (12). Prepared according to *General Procedure A* from 4-cyclohexylpyrimidine to give the title compound (71 mg, 37%).

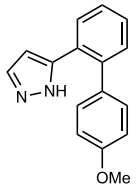
Physical properties: colorless oil
R_f = 0.21 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (d, *J* = 1.5 Hz, 1H), 8.61 (d, *J* = 5.3 Hz, 1H), 7.17 (dd, *J* = 5.3, 1.4 Hz, 1H), 2.65 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.95 (ddt, *J* = 12.3, 3.6, 1.8 Hz, 2H), 1.86 (ddd, *J* = 9.6, 5.0, 2.0 Hz, 2H), 1.76 (dtt, *J* = 12.6, 3.2, 1.5 Hz, 1H), 1.57 – 1.27 (m, 5H).

The spectrum matched that which was previously reported in the literature.[1]



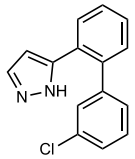
***N*,*N*-dimethyl-2'-(1*H*-pyrazol-5-yl)-[1,1'-biphenyl]-4-amine (13).** Prepared according to *General Procedure D* from *N*,*N*-dimethyl-2'-(pyrimidin-4-yl)-[1,1'-biphenyl]-4-amine to give the title compound (11 mg, 40%).

Physical properties: dark yellow oil
R_f = 0.21 (silica gel, 5% methanol/dichloromethane)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.58 (m, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.33 (m, 3H), 7.15 – 7.08 (m, 2H), 6.74 – 6.66 (m, 2H), 6.24 (s, 1H), 2.98 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 150.02, 140.43, 131.17, 130.04, 129.33, 128.51, 128.46, 127.18, 112.48, 105.20, 40.56.
HRMS (ESI): calculated for $C_{17}H_{18}N_3^+$ [M + H^+] 264.1495; found 264.1496.



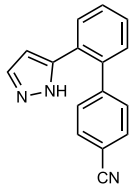
5-(4'-methoxy-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (14). Prepared according to *General Procedure D* from 4-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyrimidine to give the title compound (14.4 mg, 65%).

Physical properties: bright yellow oil
R_f = 0.23 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.56 (m, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.21 – 7.12 (m, 2H), 6.93 – 6.83 (m, 2H), 6.10 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.05, 140.02, 136.19, 133.29, 130.91, 130.35, 129.34, 128.40, 127.47, 113.91, 105.54, 55.27.
HRMS (ESI): calculated for $C_{16}H_{15}N_2O^+$ [M + H^+] 252.1179; found 252.0698.



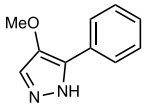
5-(3'-chloro-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (16). Prepared according to *General Procedure D* from 4-(3'-chloro-[1,1'-biphenyl]-2-yl)pyrimidine to give the title compound (8.4 mg, 33%).

Physical properties: white solid
R_f = 0.32 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.57 (m, 1H), 7.52 – 7.39 (m, 3H), 7.39 – 7.30 (m, 1H), 7.32 – 7.18 (m, 4H), 7.08 (dt, *J* = 7.6, 1.4 Hz, 1H), 5.98 (d, *J* = 2.1 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.05, 139.12, 134.14, 130.59, 129.55, 129.48, 129.36, 128.44, 128.20, 127.61, 127.40, 105.93.
HRMS (ESI): calculated for $C_{15}H_{12}ClN_2^+$ [M + H$^+$] 255.0684; found 255.0684.



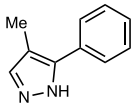
5-(4'-cyano-[1,1'-biphenyl]-2-yl)-1*H*-pyrazole (17). Prepared according to *General Procedure D* from 2'-(pyrimidin-4-yl)-[1,1'-biphenyl]-4-carbonitrile to give the title compound (11.8 mg, 49 %).

Physical properties: red solid
R_f = 0.24 (silica gel, 20% acetone/hexanes)
1H NMR
13C NMR
HRMS (ESI): calculated for $C_{16}H_{12}N_3^+$ [M + H^+] 246.1026; found 246.1028.



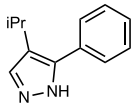
4-methoxy-5-phenyl-1*H*-pyrazole (19). Prepared according to *General Procedure D* from 5-methoxy-4-phenylpyrimidine to give the title compound (10 mg, 60%).

Physical properties: yellow solid
R_f = 0.20 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 2H), 7.31 (d, *J* = 2.5 Hz, 1H), 6.89 (td, *J* = 4.6, 2.7 Hz, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 3.85 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.99, 149.22, 133.43, 133.07, 129.87, 118.30, 113.92, 111.10, 102.91, 66.38, 55.32, 54.99.
HRMS (ESI): calculated for $C_{10}H_{11}N_2O^+$ [M + H^+] 175.0866; found 175.0866.



4-methyl-5-phenyl-1*H*-pyrazole (20). Prepared according to *General Procedure D* from 5-methyl-4-phenylpyrimidine to give the title compound (14 mg, 88%).

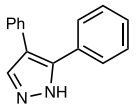
Physical properties: white solid
R_f = 0.23 (silica gel, 20% acetone/hexanes)
1H NMR
13C NMR
HRMS (ESI): calculated for $C_{10}H_{11}N_2^+$ [M + H^+] 159.0917; found 159.0916.



4-isopropyl-5-phenyl-1*H*-pyrazole (21). Prepared according to *General Procedure A* from 5-isoproyl-4-phenyl pyrimidine to give the title compound (4.5 mg, 24%).

Physical properties: colorless oil
R_f = 0.22 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.35 (m, 7H), 3.09 (hept, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H).

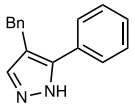
The spectrum matched that which was previously reported in the literature.[28]



4,5-diphenyl-1*H*-pyrazole (22). Prepared according to *General Procedure A* from 4,5-diphenyl pyrimidine to give the title compound (15.5 mg, 70%).

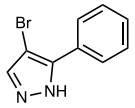
Physical properties: white solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.40 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.30 (d, *J* = 3.2 Hz, 3H), 7.26 (d, *J* = 4.4 Hz, 4H), 7.24 – 7.16 (m, *J* = 4.0 Hz, 2H).

The spectrum matched that which was previously reported in the literature.[28]



4-benzyl-5-phenyl-1*H*-pyrazole (23). Prepared according to *General Procedure D* from 5-benzyl-4-phenylpyrimidine to give the title compound (13.4 mg, 57 %).

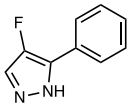
Physical properties: yellow oil
R_f = 0.35 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.61 (s, 1H), 7.80 – 7.36 (m, 5H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.22 (dd, *J* = 8.3, 6.0 Hz, 1H), 7.07 – 6.95 (m, 2H), 4.09 (s, 2H).
13C NMR
HRMS (ESI): calculated for $C_{16}H_{15}N_2^+$ [M + H^+] 235.1230; found 235.1228.



4-bromo-5-phenyl-1*H*-pyrazole (24). Prepared according to *General Procedure D* from 5-bromo-4-phenylpyrimidine to give the title compound (6.5 mg, 29%).

Physical properties: dark yellow solid
R_f = 0.19 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.68 (m, 2H), 7.64 (s, 1H), 7.56 – 7.37 (m, 3H).

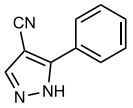
The spectrum matched that which was previously reported in the literature.[29]



4-fluoro-5-phenyl-1*H*-pyrazole (25). Prepared according to *General Procedure D* from 5-fluoro-4-phenylpyrimidine to give the title compound (2.5 mg, 15%).

Physical properties: dark yellow oil
R_f = 0.14 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 4.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 1H).

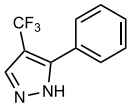
The spectrum matched that which was previously reported in the literature.[30]



4-cyano-5-phenyl-1*H*-pyrazole (26). Prepared according to *General Procedure D* from 5-cyano-4-phenylpyrimidine to give the title compound (1.9 mg, 11 %).

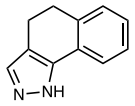
Physical properties: yellow solid
R_f = 0.15 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 4.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 1H).

The spectrum matched that which was previously reported in the literature.[31]



5-phenyl-4-(trifluoromethyl)-1*H*-pyrazole (27). Prepared according to *General Procedure D* from 4-phenyl-5-trifluoromethyl pyrimidine to give the title compound (1.8 mg, 9%).

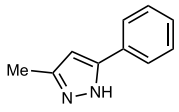
Physical properties: pale yellow solid
R_f = 0.20 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 4.5 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.33 (m, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 128.91, 128.37, 125.81, 125.78.
^{19}F NMR (470 MHz, $CDCl_3$): δ -176.97.
HRMS (ESI): calculated for $C_{10}H_8F_3N_2^+$ [M + H^+] 213.0634; found 213.0634.



4,5-dihydro-1*H*-benzo[*g*]indazole (28). Prepared according to *General Procedure D* from 5,6-dihydrobenzo[*h*]quinazoline to give the title compound (15.7 mg, 88%).

Physical properties: yellow solid
R_f = 0.31 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.34 (s, 1H), 7.95 – 7.60 (m, 1H), 7.41 (s, 1H), 7.34 – 7.13 (m, 3H), 2.96 (dd, *J* = 8.3, 6.3 Hz, 2H), 2.81 (dd, *J* = 8.3, 6.3 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 136.81, 128.48, 127.69, 126.87, 121.97, 29.74, 19.21.

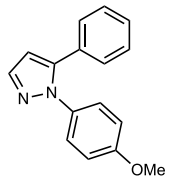
The spectra matched those which were previously reported in the literature.[32]



3-methyl-5-phenyl-1*H*-pyrazole (29). Prepared according to *General Procedure A* from 4-methyl-6-phenylpyrimidine to give the title compound (8.1 mg, 51%).

Physical properties: yellow solid
R_f = 0.16 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.62 (m, 2H), 7.39 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.36 – 7.28 (m, 1H), 6.36 (s, 1H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.97, 143.20, 132.34, 128.76, 127.96, 125.61, 102.17, 67.38, 48.62, 29.71, 11.77.

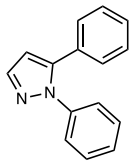
The spectrum matched that which was previously reported in the literature.[33]



1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrazole (30). Prepared according to *General Procedure E* from 4-phenylpyrimidine and (*para*-methoxy)phenylhydrazine hydrochloride to give the title compound (5.5 mg, 35%).

Physical properties: light orange solid
R_f = 0.25 (silica gel, 10% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 – 7.87 (m, 2H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.42 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.02 – 6.95 (m, 2H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H).

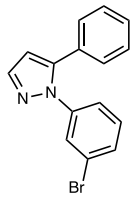
The spectrum matched that which was previously reported in the literature.[34]



1,5-diphenyl-1*H*-pyrazole (31). Prepared according to *General Procedure E* from 4-phenylpyrimidine and phenylhydrazine hydrochloride to give the title compound (9.8 mg, 45%).

Physical properties: light orange solid
R_f = 0.47 (silica gel, 10% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 – 7.86 (m, 3H), 7.86 – 7.71 (m, 2H), 7.46 (dt, *J* = 17.3, 7.6 Hz, 4H), 7.32 (dt, *J* = 24.0, 7.2 Hz, 2H), 6.78 (d, *J* = 2.5 Hz, 1H).

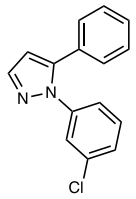
The spectra matched those which were previously reported in the literature.



1-(3-bromophenyl)-5-phenyl-1H-pyrazole (32a). Prepared according to *General Procedure E* from 4-phenylpyrimidine and (*meta*-bromo)phenylhydrazine hydrochloride to give the title compound (9.1 mg, 38%).

Physical properties: light orange solid
R_f = 0.51 (silica gel, 10% EtOAc/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.59 (t, *J* = 1.9 Hz, 1H), 7.42 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.38 – 7.29 (m, 3H), 7.24 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.19 – 7.10 (m, 2H), 6.51 (d, *J* = 1.8 Hz, 1H).

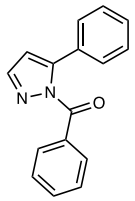
The spectrum matched that which was reported in the literature.[35]



1-(3-chlorophenyl)-5-phenyl-1H-pyrazole (32b). Prepared according to *General Procedure E* from 4-phenylpyrimidine and (*meta*-chloro)phenylhydrazine hydrochloride to give the title compound (3.7 mg, 19%).

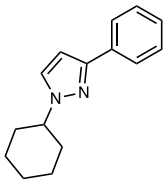
Physical properties: light orange solid
R_f = 0.45 (silica gel, 10% EtOAc/hexanes)
^{1}H NMR (700 MHz, $CDCl_3$): δ 7.72 (d, *J* = 1.7 Hz, 1H), 7.42 (t, *J* = 1.8 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 1.8 Hz, 1H).

The spectrum matched that which was reported in the literature.[35]



phenyl(5-phenyl-1*H*-pyrazol-1-yl)methanone (33). Prepared according to *General Procedure A* from 4-phenylpyrimidine and benzohydrazide to give the title compound as a solid (12.3 mg, 50%).

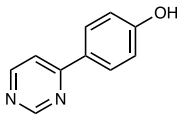
Physical properties: white solid
R_f = 0.30 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.26 (d, *J* = 1.4 Hz, 1H), 8.76 (d, *J* = 5.4 Hz, 1H), 8.13 – 8.02 (m, 3H), 7.74 (dd, *J* = 5.4, 1.4 Hz, 1H), 7.62 – 7.46 (m, 5H), 6.21 (s, 1H).
HRMS (ESI): calculated for $C_{16}H_{13}N_2O^+$ [M + H^+] 249.1022; found 249.1047.



1-cyclohexyl-3-phenyl-1*H*-pyrazole (34). Prepared according to *General Procedure E* from 4-phenylpyrimidine and cyclohexylhydrazine hydrochloride to give the title compound (11.8 mg, 52%).

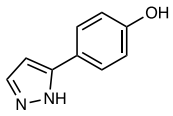
Physical properties: white solid
R_f = 0.57 (silica gel, 10% EtOAc/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 – 7.74 (m, 2H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.38 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 4.17 (tt, *J* = 11.8, 3.8 Hz, 1H), 2.27 – 2.17 (m, 2H), 1.91 (dt, *J* = 13.6, 3.5 Hz, 2H), 1.73 (qd, *J* = 12.4, 4.0 Hz, 3H), 1.45 (qt, *J* = 13.2, 3.5 Hz, 2H), 1.35 – 1.21 (m, 2H).

The spectrum matched that which was reported in the literature.[36]



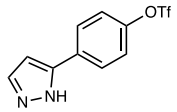
4-(pyrimidin-4-yl)phenol (S40). Prepared according to *General Procedure A* from 4-hydroxyacetophenone acid to give the title compound (79 mg, 46%)

Physical properties: pale yellow solid
R_f = 0.46 (silica gel, 50% acetone in hexanes)
^{1}H NMR (500 MHz, Acetone): δ 9.10 (d, *J* = 1.4 Hz, 1H), 8.95 (s, 1H), 8.71 (d, *J* = 5.4 Hz, 1H), 8.17 – 8.11 (m, 2H), 7.88 (dd, *J* = 5.5, 1.4 Hz, 1H), 7.04 – 6.95 (m, 2H).
^{13}C NMR (126 MHz, Acetone) δ 205.25, 163.00, 160.39, 158.81, 157.37, 128.78, 127.84, 115.75.
HRMS (ESI): calculated for $C_{10}H_9N_2O^+$ [M + H^+] 173.0709; found 173.0667.



4-(1*H*-pyrazol-5-yl)phenol (35). Prepared according to *General Procedure D* using 3.0 equiv Tf_2O, 4.0 equiv Na_2CO_3, and 3.0 equiv H_2NNH_2 from 4-(pyrimidin-4-yl)phenol (**S40**) to give the title compound (10.4 mg, 65%)

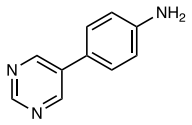
Physical properties: white solid
R_f = 0.47 (silica gel, 50% acetone in hexanes)
^{1}H NMR (400 MHz, Acetone): δ 8.43 (s, 1H), 7.72 – 7.65 (m, 2H), 7.64 (d, *J* = 2.2 Hz, 1H), 6.92 – 6.85 (m, 2H), 6.56 (d, *J* = 2.2 Hz, 1H).
^{13}C NMR (126 MHz, Acetone): δ 157.08, 126.69, 126.55, 115.36, 100.90, 59.65, 13.60.
HRMS (ESI): calculated for $C_9H_9N_2O^+$ [M + H^+] 161.0709; found 161.0710.



4-(1H-pyrazol-5-yl)phenyl trifluoromethanesulfonate (36). Prepared according to *General Procedure D* using 3.0 equiv Tf_2O, 4.0 equiv Na_2CO_3, and 3.0 equiv H_2NNH_2 from 4-(pyrimidin-4-yl)phenol (**S40**) to give the title compound (31 mg, 61%)

Physical properties: white solid
R_f = 0.81 (silica gel, 50% acetone in hexanes)
^{1}H NMR (400 MHz, Acetone): δ 8.14 – 7.96 (m, 2H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.39 (m, 2H), 6.80 (d, *J* = 2.3 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.09, 133.23, 131.55, 127.53, 122.60, 121.72, 120.05, 117.50, 114.95, 103.11, 67.35, 48.61, 30.95, 29.28.
^{19}F NMR (470 MHz, $CDCl_3$): δ -72.77, -72.79, -73.26.

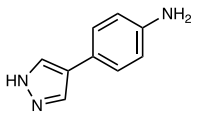
HRMS (ESI): calculated for $C_{10}H_8F_3N_2O_3S^+$ [M + H^+] 293.0202; found 294.01179.



4-(pyrimidin-5-yl)aniline (S41). Prepared from 5-bromopyrimidine and (4-aminophenyl)boronic acid according to *General Procedure C* to give the title compound (80 mg, 96%)

Physical properties: pale yellow solid
R_f = 0.32 (silica gel, 67% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (s, 1H), 8.89 (s, 2H), 7.49 – 7.32 (m, 2H), 6.89 – 6.69 (m, 2H), 3.84 (s, 1H).

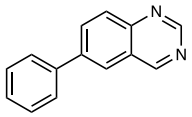
The spectra matched those which were previously reported in the literature.[37]



4-(1H-pyrazol-4-yl)aniline (37). Prepared from *General Procedure D* using 3.0 equiv Tf_2O, 4.0 equiv Na_2CO_3, and 3.0 equiv H_2NNH_2 from (**S41**) to give the title compound (7.5 mg, 47%)

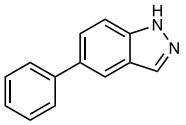
Physical properties: amber solid
R_f = 0.24 (silica gel, 50% acetone in hexanes)
^{1}H NMR (500 MHz, Acetone) δ 11.92 (s, 1H), 7.79 (s, 2H), 7.39 – 7.17 (m, 2H), 6.82 – 6.56 (m, 2H), 4.54 (s, 1H).

The spectrum matched that which was previously reported in the literature.[38]



6-phenylquinazoline (S42). Prepared according to *General Procedure E* from 6-bromoquinazoline and phenylboronic acid to give the title compound (197 mg, 96%)

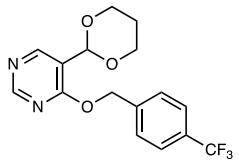
Physical properties: white solid
R_f = 0.50 (silica gel, 50% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 9.35 (d, *J* = 1.3 Hz, 1H), 8.21 (dt, *J* = 8.9, 1.7 Hz, 1H), 8.18 – 8.07 (m, 2H), 7.75 – 7.68 (m, 2H), 7.57 – 7.49 (m, 2H), 7.45 (td, *J* = 7.4, 1.4 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.43, 155.24, 149.43, 140.97, 139.45, 134.00, 129.20, 128.91, 128.34, 127.48, 125.39, 124.61.
HRMS (ESI): calculated for $C_{14}H_{11}N_2^+$ [M + H^+] 207.0917; found 206.0844.



5-phenyl-1*H*-indazole (38). Prepared from 6-phenylquinazoline according to *General Procedure D* to give the title compound (8.0 mg, 41%)

Physical properties: bright yellow solid
R_f = 0.47 (silica gel, 50% acetone in hexanes)
^{1}H NMR (500 MHz, Acetone): δ 8.60 (s, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.49 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.29 – 7.20 (m, 1H), 6.94 – 6.88 (m, 2H).
^{13}C NMR (126 MHz, Acetone) δ 165.64, 161.99, 148.47, 140.63, 131.79, 129.61, 128.70, 128.21, 126.03, 125.74, 115.94, 115.85, 24.35, 17.62.

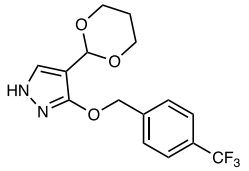
The spectra matched those which were previously reported in the literature.[39]



5-(1,3-dioxan-2-yl)-4-((4-(trifluoromethyl)benzyl)oxy)pyrimidine (benzpyrimoxan, 39). Prepared according to a previously reported protocol[40] to give the title compound (470 mg, 42%)

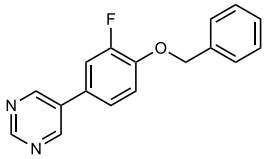
Physical properties: yellow solid
R_f = 0.24 (silica gel, 30% ethyl acetate in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 5.55 (s, 2H), 4.27 (ddd, *J* = 12.0, 5.1, 1.4 Hz, 2H), 3.99 (td, *J* = 12.3, 2.3 Hz, 2H), 2.25 (qt, *J* = 12.6, 5.0 Hz, 1H), 1.47 (ddd, *J* = 13.0, 3.2, 1.8 Hz, 1H).

The spectrum matched that which was previously reported in the literature.[40]



4-(1,3-dioxan-2-yl)-3-((4-(trifluoromethyl)benzyl)oxy)-1H-pyrazole (S43). Prepared according to *General Procedure D* at 60 ˚C from 5-(1,3-dioxan-2-yl)-4-((4-(trifluoromethyl)benzyl)oxy)pyrimidine (benzpyrimoxan) to give the title compound (6.6 mg, 20%)

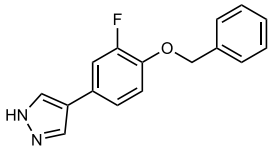
Physical properties: white solid
R_f = 0.23 (silica gel, 20% acetone in hexanes)
^{1}H NMR (500 MHz, Acetone): δ 8.62 (s, 1H), 8.06 (s, 1H), 7.77 – 7.67 (m, 2H), 7.67 – 7.61 (m, 2H), 5.62 (s, 1H), 5.31 (s, 2H), 4.19 – 4.06 (m, 2H), 4.01 – 3.85 (m, 2H), 2.81 (s, 3H).
^{13}C NMR (126 MHz, Acetone): δ 205.27, 158.92, 152.22, 150.92, 140.97, 131.82, 129.58, 128.75, 128.58, 128.48, 125.58, 125.54, 125.51, 125.48, 125.43, 95.63, 67.13, 49.16, 29.50, 25.68.
^{19}F NMR (470 MHz, Acetone) δ -63.11.
HRMS (ESI): calculated for $C_{15}H_{16}F_3N_2O_3^+$ [M + H^+] 329.1108; found 329.1112.



5-(4-(benzyloxy)-3-fluorophenyl)pyrimidine (40). Prepared from 5-bromopyrimidine and (4-(benzyloxy)-3-fluorophenyl)boronic acid to give the title compound (117 mg, 66%).

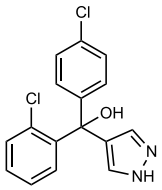
Physical properties: white solid
R_f = 0.31 (silica gel, 50% acetone in hexanes)
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.89 (s, 2H), 7.46 (dddd, *J* = 7.9, 2.5, 1.6, 0.9 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H), 7.27 (dd, *J* = 2.3, 1.2 Hz, 1H), 7.13 (t, *J* = 8.4 Hz, 1H), 5.22 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.41, 154.51, 136.05, 128.74, 128.34, 127.42, 122.84, 116.36, 114.93, 114.80, 71.42.

The spectra matched those which were previously reported in the literature.



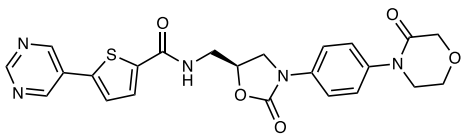
4-(4-(benzyloxy)-3-fluorophenyl)-1*H*-pyrazole (S44). Prepared according to *General Procedure D* from **5-(4-(benzyloxy)-3-fluorophenyl)pyrimidine** to give the title compound (15.3 mg, 57%).

Physical properties: white solid
R_f = 0.12 (silica gel, 20% acetone in hexanes)
^{1}H NMR (500 MHz, Acetone): δ 8.28 – 7.75 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.42 (dt, *J* = 15.1, 5.0 Hz, 3H), 7.39 – 7.29 (m, 2H), 7.21 (t, *J* = 8.7 Hz, 1H), 5.22 (s, 2H).
^{13}C NMR (126 MHz, Acetone): δ 151.98, 144.94, 137.11, 128.44, 127.93, 127.65, 127.37, 121.15, 121.13, 116.18, 116.16, 113.18, 113.02, 70.89.
HRMS (ESI): calculated for $C_{16}H_{14}FN_2O^+$ [M + H$^+$] 269.1085; found 269.1036.



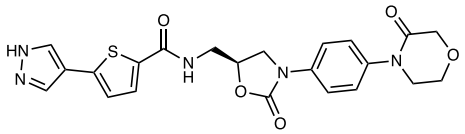
(2-Chlorophenyl)(4-chlorophenyl)(1*H*-pyrazol-4-yl)methanol (S45). Prepared from (2-chlorophenyl)(4-chlorophenyl)(pyrimidin-5-yl)methanol (Fenarimol®, **41**) according to *General Procedure D* to give the title compound (11 mg, 37%).

Physical properties: white solid
R_f = 0.08 (silica gel, 20% acetone in hexanes),
^{1}H NMR (500 MHz, DMSO): δ 12.65 (s, 1H), 7.54 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.39 – 7.26 (m, 7H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H).
^{13}C NMR (126 MHz, DMSO): δ 146.30, 144.85, 132.93, 131.70, 131.51, 129.75, 129.57, 129.08, 127.97, 126.99, 126.71, 75.88, 71.18, 70.77, 46.15, 29.47, 19.71, 18.64.
HRMS (ESI): calculated for $C_{16}H_{13}Cl_2N_2O^+$ [M + H^+] 319.0399; found 319.0225.



(*S*)-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)-5-(pyrimidin-5-yl)thiophene-2-carboxamide (42). Prepared from Rivaroxaban® and pyrimidin-5-yl boronic acid to give the title compound (207 mg, 43%).

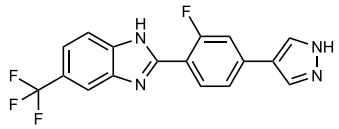
Physical properties: white solid
R_f = 0.25 (silica gel, 5% MeOH in CH_2Cl_2)
^{1}H NMR (500 MHz, DMSO): δ 9.15 (s, 2H), 9.14 (s, 1H), 9.01 (t, *J* = 5.9 Hz, 1H), 7.86 (d, *J* = 4.0 Hz, 1H), 7.76 (d, *J* = 3.9 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.38 (d, *J* = 9.0 Hz, 2H), 4.85 (dd, *J* = 8.8, 5.6 Hz, 1H), 4.20 (d, *J* = 9.1 Hz, 1H), 4.16 (s, 2H), 3.97 – 3.90 (m, 2H), 3.85 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.71 – 3.65 (m, 2H), 3.62 (t, *J* = 5.6 Hz, 2H).
^{13}C NMR (126 MHz, DMSO) δ 165.97, 161.36, 157.67, 154.13, 153.54, 140.69, 140.06, 137.07, 136.51, 129.49, 127.48, 126.93, 125.96, 118.35, 71.38, 67.73, 67.35, 63.47, 49.01, 47.47, 21.48.
HRMS (ESI): calculated for $C_{23}H_{22}N_5O_5S^+$ [M + H^+] 480.1336; found 480.1141.



(*S*)-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)-5-(1*H*-pyrazol-4-yl)thiophene-2-carboxamide (S46). Prepared from (*S*)-*N*-((2-oxo-3-(4-(3-oxomorpholino)phenyl)oxazolidin-5-yl)methyl)-5-(pyrimidin-5-yl)thiophene-2-carboxamide (**54**) according to *General Procedure D* in HFIP instead of dioxane to give the title compound (8.0 mg, 17%).

The HFIP (purchased from Oakwood) used for this reaction was distilled under an atmosphere of nitrogen into a flame-dried Schlenk tube containing activated 3 Å molecular sieves, over which the solvent was dried under an atmosphere of nitrogen for 24 h prior to use.

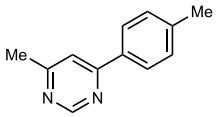
Physical properties: white solid
R_f = 0.11 (silica gel, 5% MeOH in CH_2Cl_2), fluorescent spot
^{1}H NMR (500 MHz, DMSO): δ 13.11 (s, 1H), 8.79 (t, *J* = 5.9 Hz, 1H), 8.17 (s, 1H), 7.81 (d, *J* = 24.7 Hz, 1H), 7.71 (d, *J* = 3.9 Hz, 1H), 7.65 – 7.47 (m, 2H), 7.47 – 7.33 (m, 2H), 7.22 (d, *J* = 3.8 Hz, 1H), 4.85 (dq, *J* = 8.9, 5.6 Hz, 1H), 4.19 (d, *J* = 3.9 Hz, 3H), 3.96 (dd, *J* = 6.0, 4.2 Hz, 2H), 3.87 (dd, *J* = 9.1, 6.1 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.61 (t, *J* = 5.6 Hz, 2H).
^{13}C NMR (126 MHz, DMSO): δ 166.44, 162.28, 154.65, 154.62, 140.93, 137.54, 137.00, 135.99, 129.76, 126.43, 123.29, 118.83, 115.38, 71.90, 68.20, 63.94, 49.49, 47.94, 42.67.
HRMS (ESI): calculated for $C_{22}H_{22}N_5O_5S^-$ [M – H$^+$] 466.1185; found 466.1192.



2-(2-fluoro-4-(1*H*-pyrazol-4-yl)phenyl)-5-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (S47). Prepared from (2-(2-fluoro-4-(2-(methylsulfinyl)pyrimidin-5-yl)phenyl)-5-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (**43**) according to *General Procedure D* to give the title compound (45.0 mg, 65%).

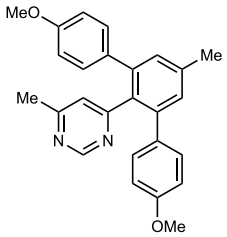
Physical properties: white solid
R_f = 0.33 (silica gel, 10% MeOH in CH_2Cl_2), fluorescent spot
^{1}H NMR (400 MHz, MeOD): δ 8.64 (s, 1H), 8.16 – 7.99 (m, 2H), 7.85 (s, 1H), 7.71 – 7.62 (m, 1H), 7.47 (tq, *J* = 23.2, 15.5, 11.9 Hz, 4H).
^{13}C NMR (126 MHz, MeOD): δ 161.66, 159.90, 159.68, 159.53, 156.04, 152.47, 130.51, 130.27, 122.76, 121.58, 121.54, 121.52, 120.31, 115.52, 115.43, 114.10, 112.84, 112.65, 112.46, 112.27, 65.86, 54.59, 29.37, 23.58, 23.26, 16.60, 15.66.
HRMS (ESI): calculated for $C_{17}H_{11}F_4N_4^+$ [M + H^+] 347.0914; found 347.0910.

This compound was found to be of extremely limited solubility in all typical organic solvents (even DMSO). Additionally, this compound was found to decompose on standing in alcoholic solvents.



4-methyl-6-(*p*-tolyl)pyrimidine (44). Prepared from 4-chloro-6-methylpyrimidine and (*o*-tolyl)boronic acid according to *General Procedure B* to give the title compound (184 mg, 99%).

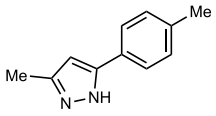
Physical properties: white solid
R_f = 0.53 (silica gel, 30% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.11 (d, *J* = 1.3 Hz, 1H), 8.06 – 7.89 (m, 2H), 7.56 (d, *J* = 1.3 Hz, 1H), 7.34 – 7.28 (m, 2H), 2.58 (s, 3H), 2.42 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.28, 163.76, 158.67, 141.28, 133.96, 129.72, 127.04, 116.11, 24.38, 21.44.
HRMS (ESI): calculated for $C_{12}H_{13}N_2^+$ [M + H^+] 185.1073; found 185.1071.



4-(4,4''-dimethoxy-5'-methyl-[1,1':3',1''-terphenyl]-2'-yl)-6-methylpyrimidine (45). Prepared from 4-methyl-6-(*o*-tolyl)pyrimidine (**45**) according to a previously reported protocol to give the title compound (149 mg, quantitative).[5]

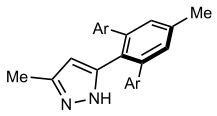
Concentration of a solution of the pure compound in ethyl acetate produced an easy to handle allotrope; other solvents, such as chloroform, acetone, and dichloromethane, caused the formation of a foam.

Physical properties: white solid
R_f = 0.19 (silica gel, 20% acetone in hexanes), 0.40 (30% acetone in hexnaes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.80 (d, *J* = 1.4 Hz, 1H), 7.22 (d, *J* = 0.8 Hz, 2H), 7.02 – 6.98 (m, 4H), 6.74 – 6.70 (m, 5H), 3.76 (s, 6H), 2.46 (s, 3H), 2.25 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.37, 158.37, 157.56, 141.20, 138.62, 133.55, 133.48, 130.53, 130.10, 123.77, 113.33, 55.20, 23.94, 21.27.
HRMS (ESI): calculated for $C_{26}H_{25}N_2O_2^+$ [M + H^+] 397.1911; found 397.1912.



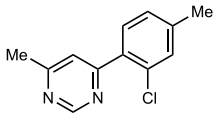
3-methyl-5-(*p*-tolyl)-1*H*-pyrazole (S48). Prepared from 4-methyl-6-(*p*-tolyl)pyrimidine (**44**) according to *General Procedure E* to give the title compound (46 mg, 98%).

Physical properties: white solid, insoluble in chloroform
R_f = 0.46 (silica gel, 30% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 – 7.52 (m, 2H), 7.23 – 7.15 (m, 2H), 6.32 (d, *J* = 0.7 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.64, 143.54, 137.80, 129.44, 129.37, 125.51, 101.95, 21.26, 11.89.
HRMS (ESI): calculated for $C_{11}H_{13}N_2^+$ [M + H^+] 173.1073; found 173.1071.



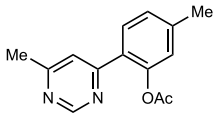
5-(4,4''-dimethoxy-5'-methyl-[1,1':3',1''-terphenyl]-2'-yl)-3-methyl-1*H*-pyrazole (46). Prepared from 4-(4,4''-dimethoxy-5'-methyl-[1,1':3',1''-terphenyl]-2'-yl)-6-methylpyrimidine (**45**) according to *General Procedure D* to give the title compound (25.6 mg, 53%).

Physical properties: white solid
R_f = 0.35 (silica gel, 30% acetone in hexanes)
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (s, 2H), 7.12 – 6.99 (m, 4H), 6.84 – 6.70 (m, 4H), 5.45 (s, 1H), 3.78 (s, 6H), 2.43 (s, 3H), 2.08 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 171.15, 158.55, 142.20, 138.31, 133.77, 130.11, 130.10, 129.89, 125.31, 113.37, 107.70, 60.39, 55.17, 53.83, 31.93, 31.73, 29.70, 29.29, 21.18, 21.04, 14.20, 14.12, 13.00.
HRMS (ESI): calculated for $C_{25}H_{25}N_2O_2^+$ [M + H^+] 385.1911; found 385.1915.



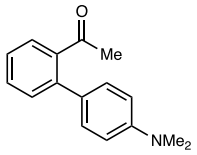
4-(2-chloro-4-methylphenyl)-6-methylpyrimidine (47). Prepared from **44** according to a previously reported directed C–H functionalization protocol[41] to give the title compound (91 mg, 78%).

Physical properties: white solid
R_f = 0.47 (silica gel, 20% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (d, *J* = 1.4 Hz, 1H), 7.58 (d, *J* = 1.4 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.20 (ddd, *J* = 7.8, 1.7, 0.9 Hz, 1H), 2.60 (s, 3H), 2.40 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 165.20, 165.08, 158.61, 141.89, 133.51, 129.83, 127.21, 114.55, 45.46, 21.48.
HRMS (ESI): calculated for $C_{12}H_{12}ClN_2^+$ [M + H^+] 219.0684.; found 219.0686.



5-methyl-2-(6-methylpyrimidin-4-yl)phenyl acetate (48). Prepared from **44** according to a previously reported directed C–H acetoxylation protocol[18] to give the title compound (122 mg, 75%).

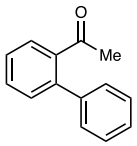
Physical properties: white solid
R_f = 0.41 (silica gel, 20% acetone in hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.9 Hz, 1H), 7.42 (s, 1H), 7.19 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 7.00 (t, *J* = 1.2 Hz, 1H), 2.57 (s, 3H), 2.42 (s, 3H), 2.24 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 169.39, 167.10, 162.87, 158.37, 148.37, 142.08, 130.37, 127.70, 127.46, 124.15, 119.59, 24.33, 21.29, 21.05.
HRMS (ESI): calculated for $C_{14}H_{15}N_2O_2^+$ [M + H^+] 243.1128.; found 243.1129.



1-(4'-(dimethylamino)-[1,1'-biphenyl]-2-yl)ethan-1-one (S49). Prepared according to *General Procedure B* to give the title compound (108 mg, 90%).

Physical properties: yellow oil
R_f = 0.40 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (ddd, *J* = 13.6, 7.5, 1.5 Hz, 2H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.34 (td, *J* = 7.5, 1.3 Hz, 1H), 7.24 – 7.19 (m, 2H), 6.77 (d, *J* = 8.3 Hz, 2H), 3.01 (s, 6H), 2.02 (s, 3H).

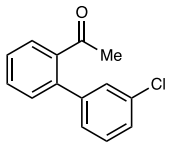
The spectrum matched that which was previously reported in the literature.[42]



1-([1,1'-biphenyl]-2-yl)ethan-1-one (S50). Prepared according to *General Procedure B* to give the title compound (193 mg, 98%).

Physical properties: yellow oil
R_f = 0.56 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 – 7.47 (m, 2H), 7.47 – 7.37 (m, 5H), 7.37 – 7.32 (m, 2H), 2.01 (s, 3H).

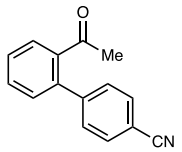
The spectrum matched that which was previously reported in the literature.[43]



1-(3'-chloro-[1,1'-biphenyl]-2-yl)ethan-1-one (S51). Prepared according to *General Procedure B* to give the title compound (133 mg, 77%).

Physical properties: yellow solid
R_f = 0.55 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.56 (m, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.19 (dt, *J* = 6.8, 1.8 Hz, 1H), 2.10 (s, 3H).

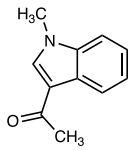
The spectrum matched that which was previously reported in the literature.[42]



1-(4'-cyano-[1,1'-biphenyl]-2-yl)ethan-1-one (S52). Prepared according to *General Procedure B* to give the title compound (105 mg, 87%).

Physical properties: yellow oil
R_f = 0.48 (silica gel, 20% acetone/hexanes)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.67 – 7.50 (m, 3H), 7.46 (td, *J* = 7.7, 1.3 Hz, 1H), 7.36 (td, *J* = 7.9, 1.2 Hz, 2H), 2.46 (s, 3H).

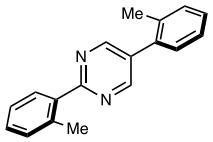
The spectra matched those which were previously reported in the literature.[44]



1-(1-methyl-1*H*-indol-3-yl)ethan-1-one (S53). Prepared from methyl iodide and 3-acetylindole with NaH to give the title compound (1.20 g, 100%).

Physical properties: pale yellow solid
R_f = 0.18 (silica gel, 20% acetone/hexanes)
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 – 8.32 (m, 1H), 7.72 (s, 1H), 7.39 – 7.27 (m, 3H), 3.86 (s, 3H), 2.53 (s, 3H).

The spectra matched those which were previously reported in the literature.[2]



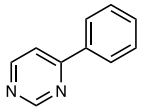
2,5-di-*o*-tolylpyrimidine (S54). Prepared according to *General Procedure E* from 2,5-dichloropyrimdine and (2-methylphenyl)boronic acid to give the title compound (105 mg, 59%)

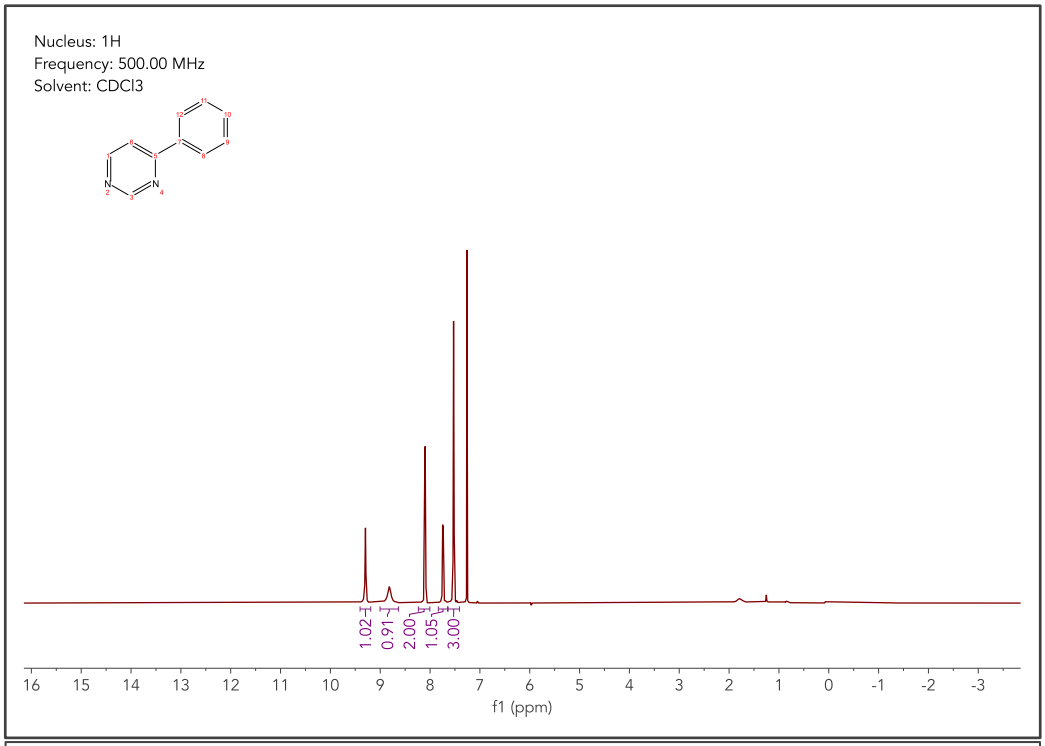
Physical properties: white solid
R_f = 0.45 (silica gel, 5% ethyl acetate in hexanes)
^{1}H NMR (500 MHz, Acetone): δ 8.91 (s, 2H), 8.02 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.42 – 7.31 (m, 7H), 2.64 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, Acetone): δ 205.23, 165.48, 156.41, 137.89, 137.54, 135.84, 134.78, 132.16, 131.29, 130.75, 130.73, 130.64, 129.94, 129.34, 128.69, 126.40, 125.69, 29.69, 20.97, 19.55.

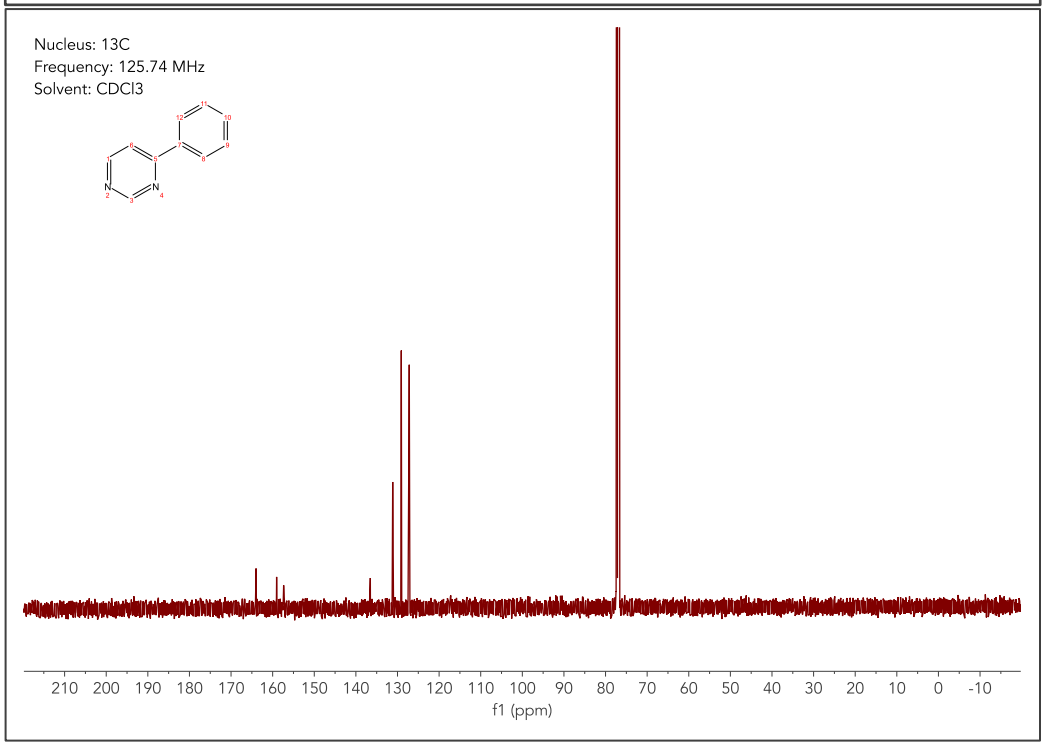
HRMS (ESI): calculated for $C_{18}H_{17}N_2^+$ [M + H^+] 261.1386; found xx.

5. ^{1}H, ^{13}C, and ^{19}F NMR Spectra

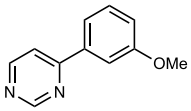
Compound **S1**

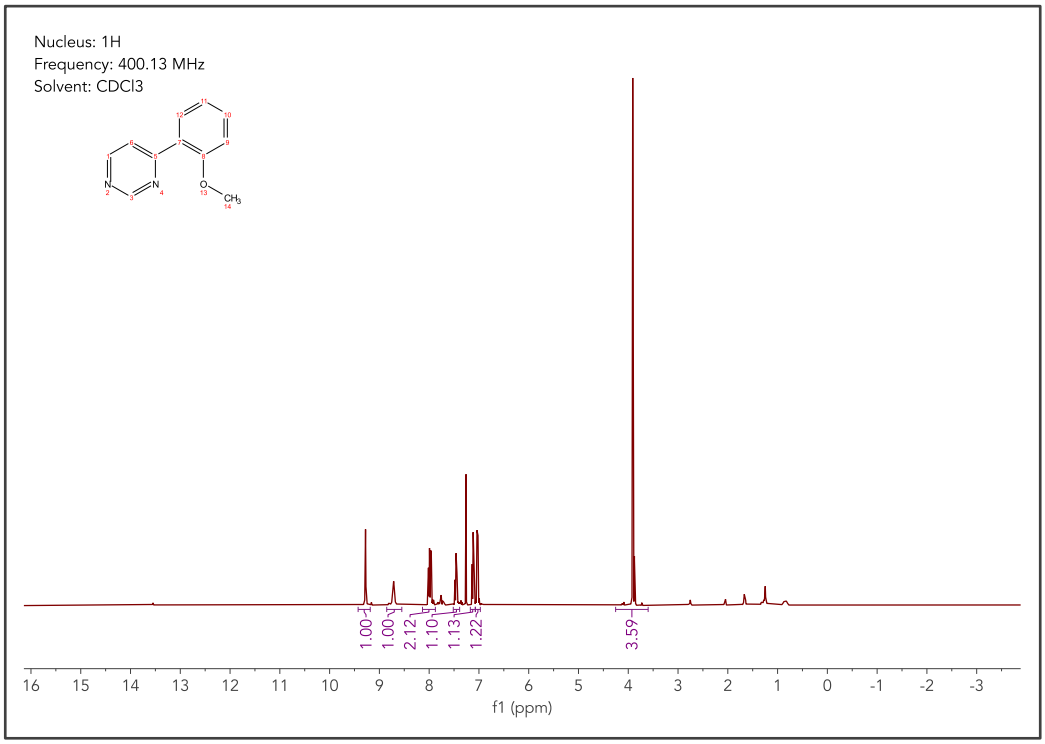




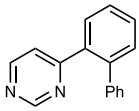


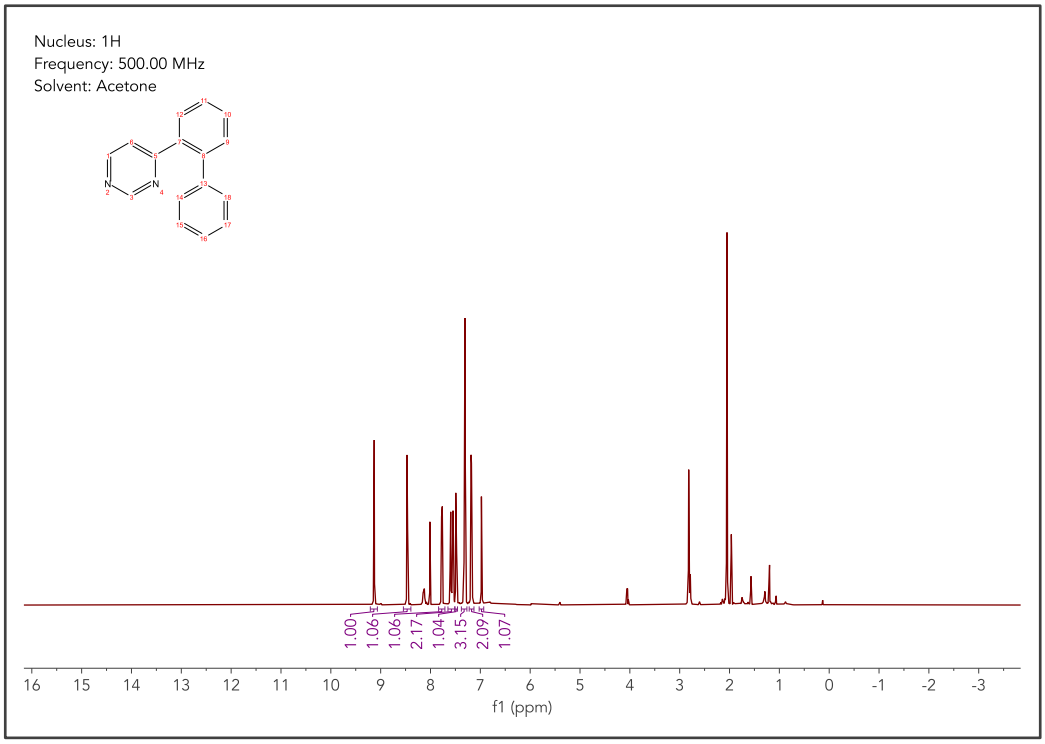
Compound **S3**


OMe
N
N

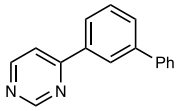

Nucleus: 1H
Frequency: 400.13 MHz
Solvent: CDCl3
1.00
1.00
2.12
1.10
1.13
1.22
3.59
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

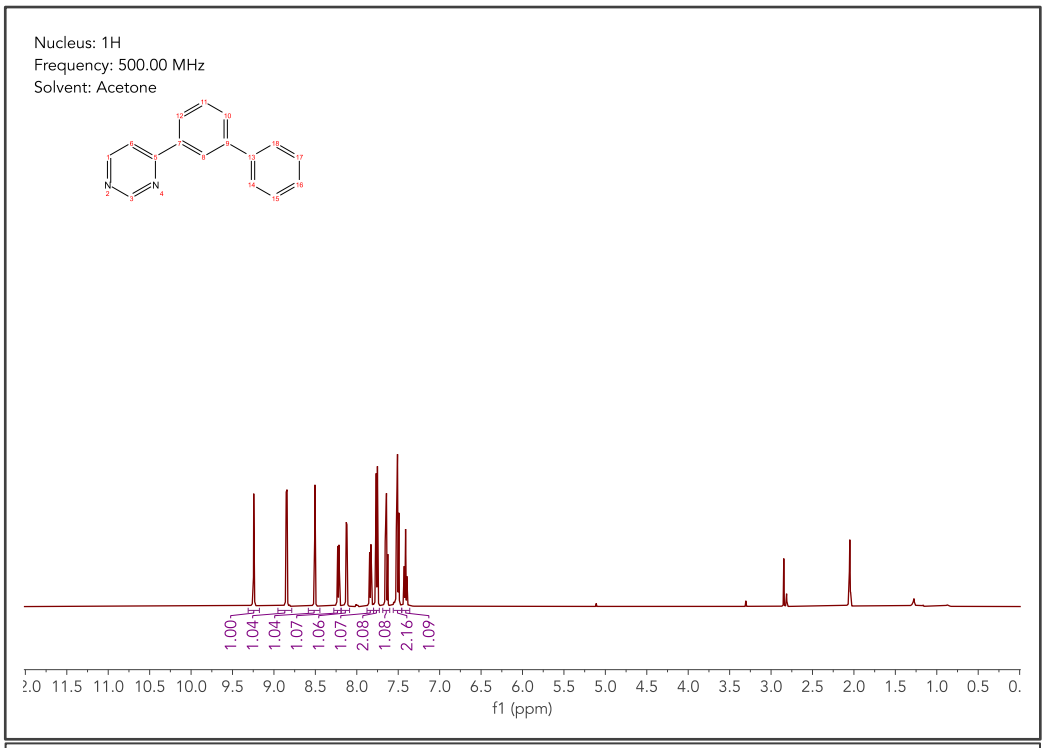
Compound **S4**

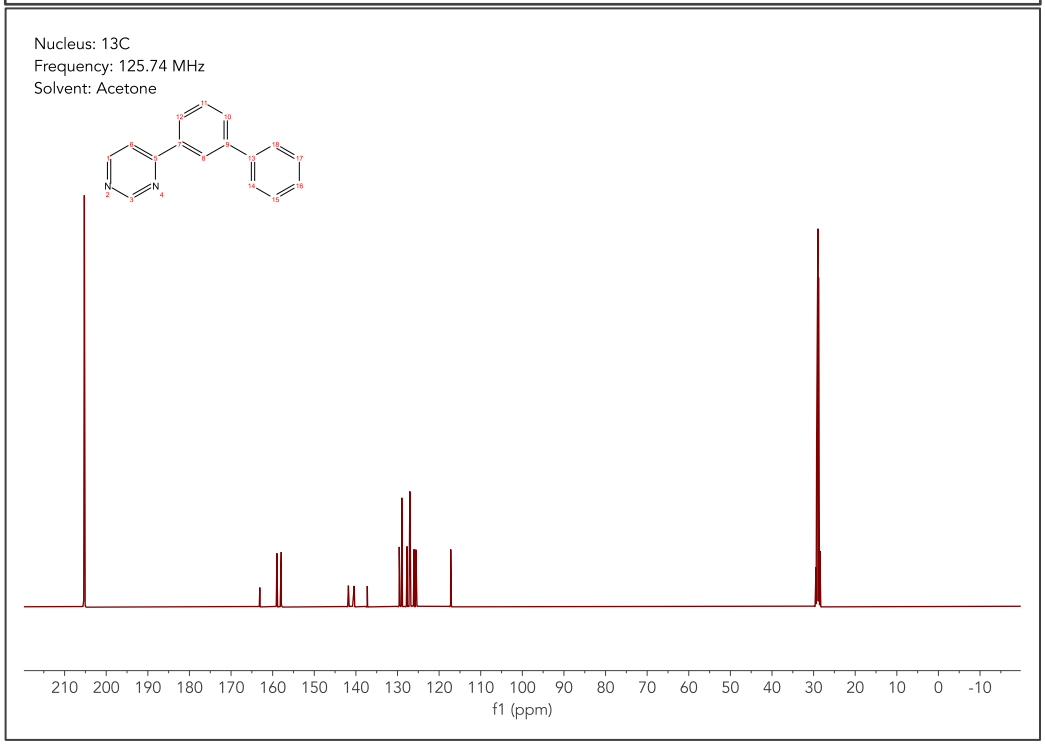

N
N
Ph


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: Acetone
1.00
1.06
1.06
2.17
1.04
3.15
2.09
1.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

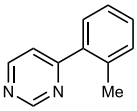
Compound **S5**

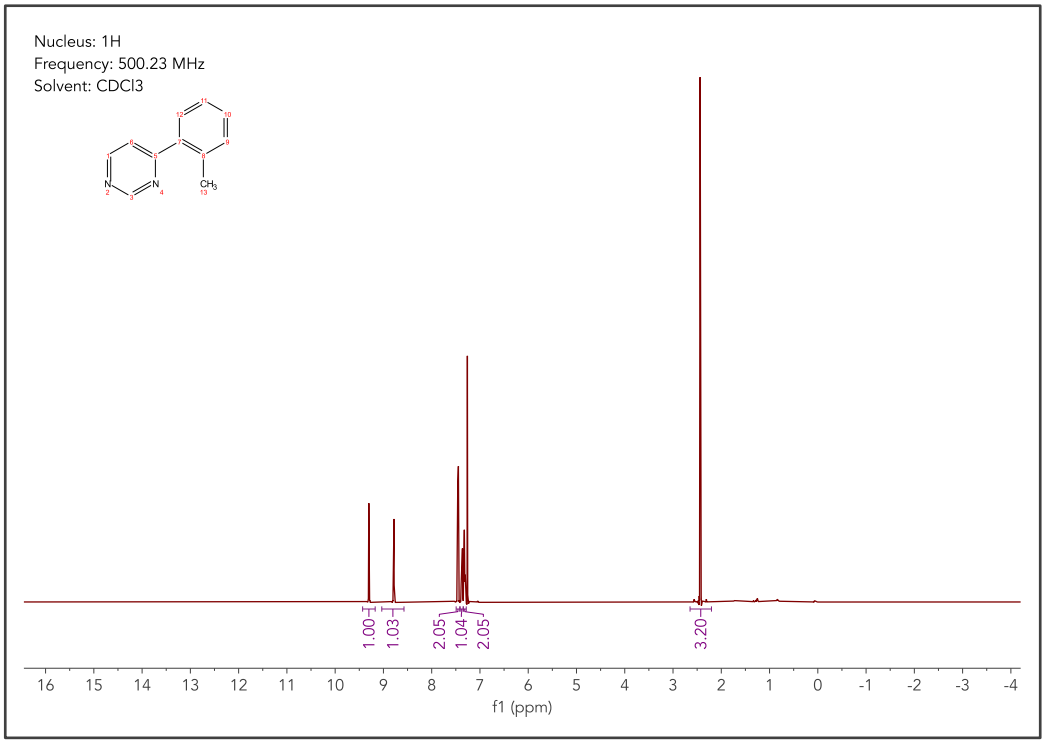

Ph
N
N


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: Acetone
1.00
1.04
1.04
1.07
1.06
1.07
2.08
1.08
2.16
1.09
f1 (ppm)

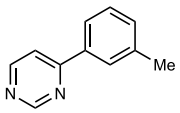

Nucleus: 13C
Frequency: 125.74 MHz
Solvent: Acetone
f1 (ppm)

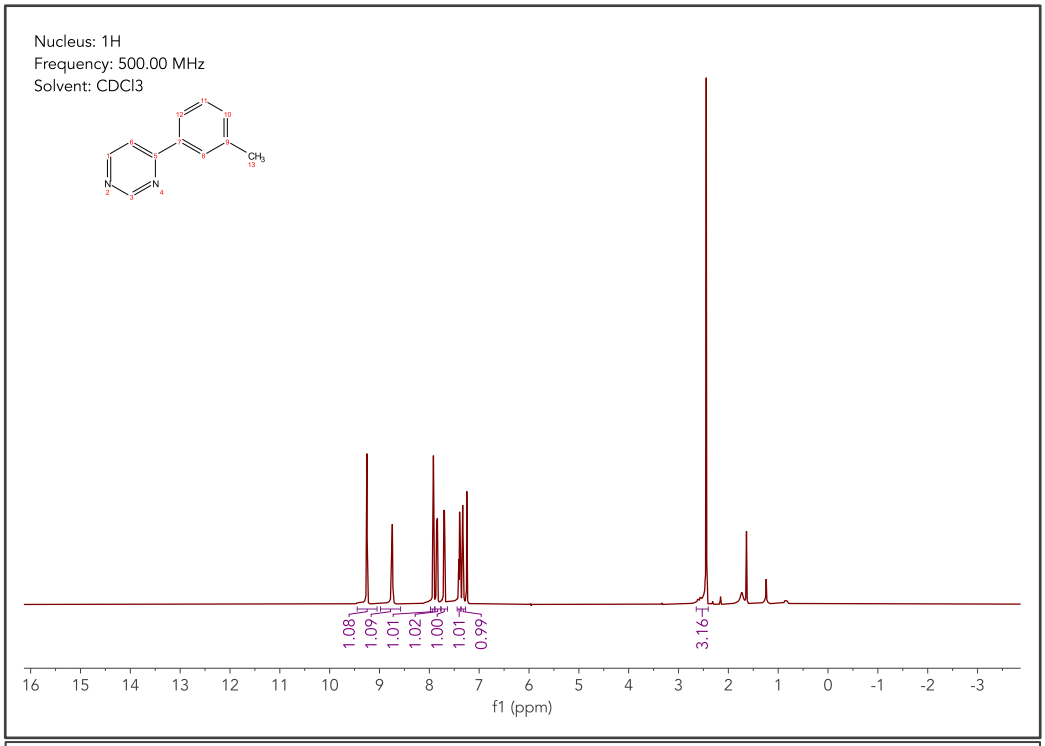
Compound **S6**

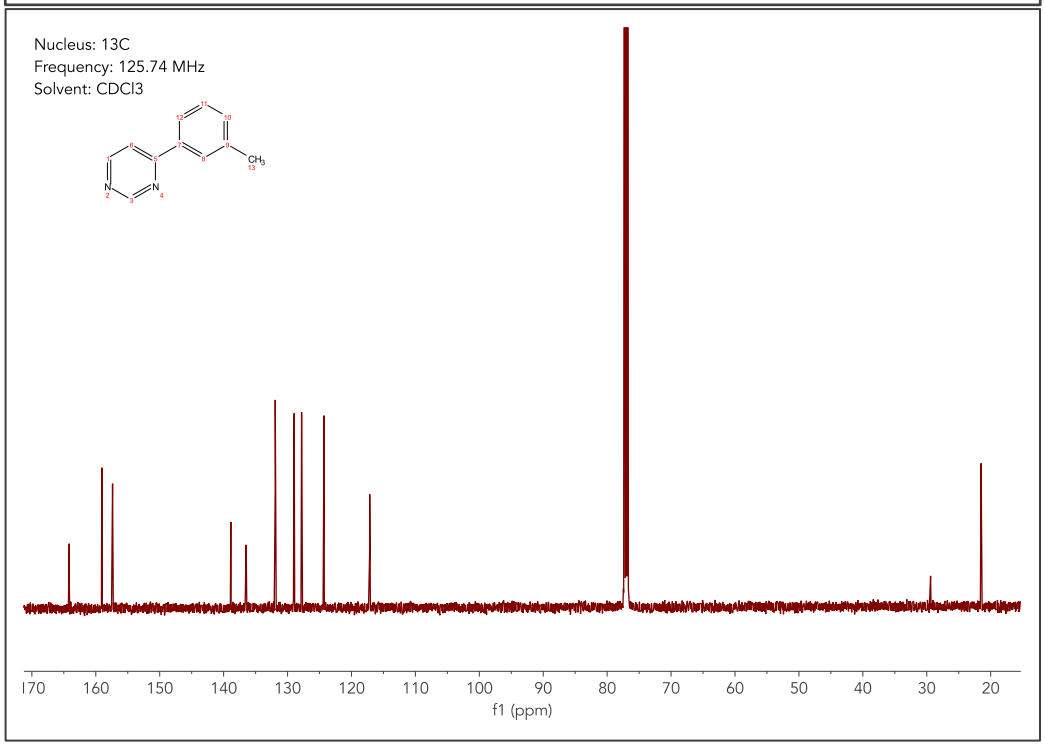

N
N
Me


Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
1.00
1.03
2.05
1.04
2.05
3.20
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

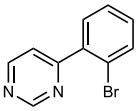
Compound **S7**

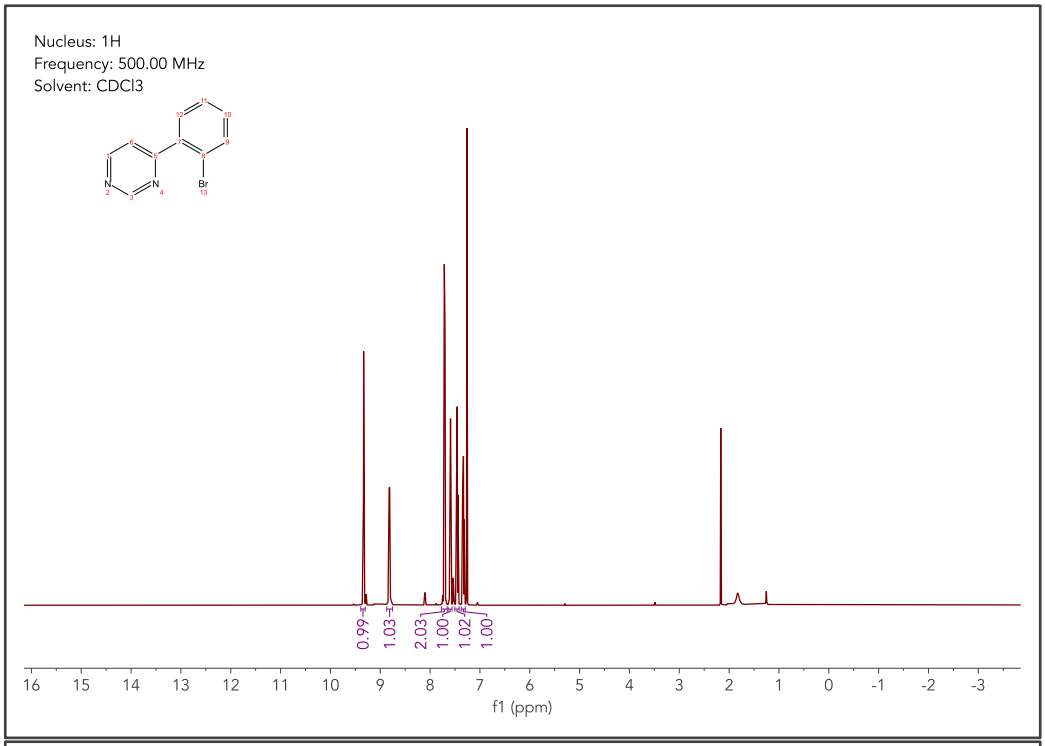

Me
N
N

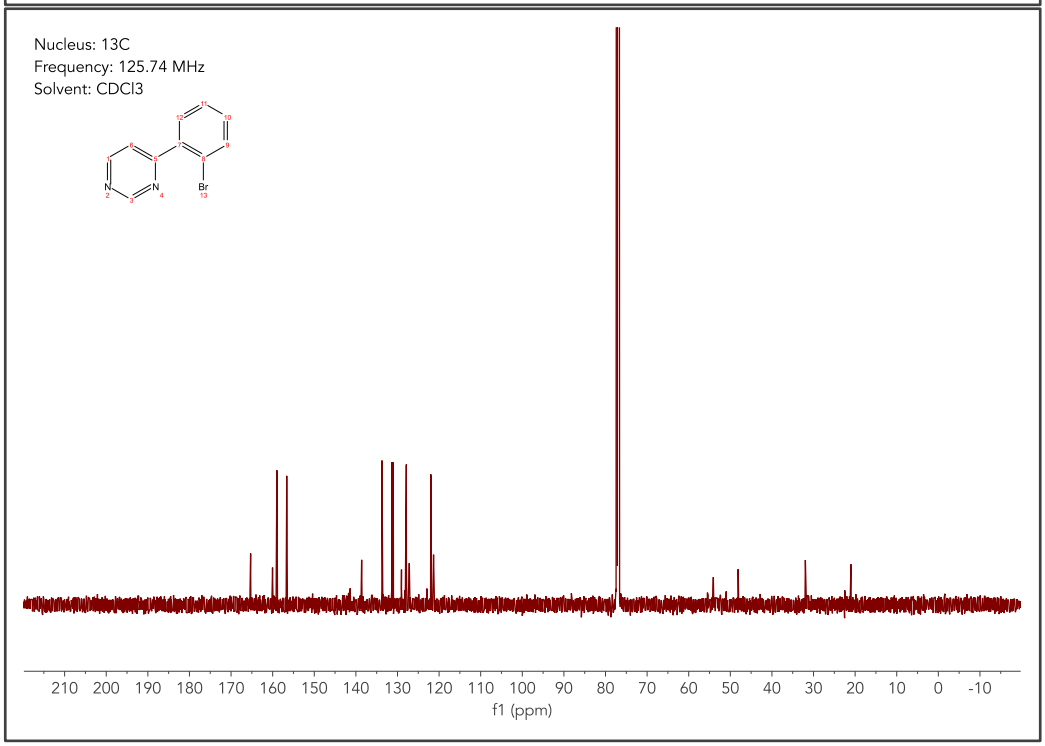

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.08
1.09
1.01
1.02
1.00
1.01
0.99
3.16
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

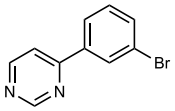
Compound **S8**

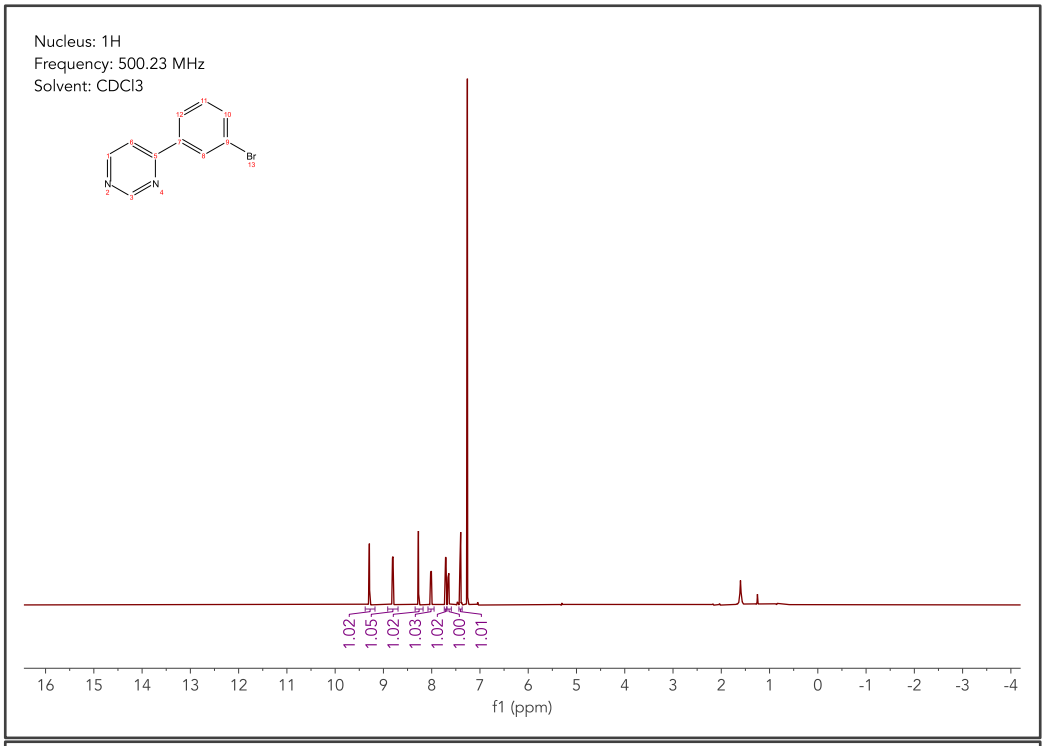

N
N
Br

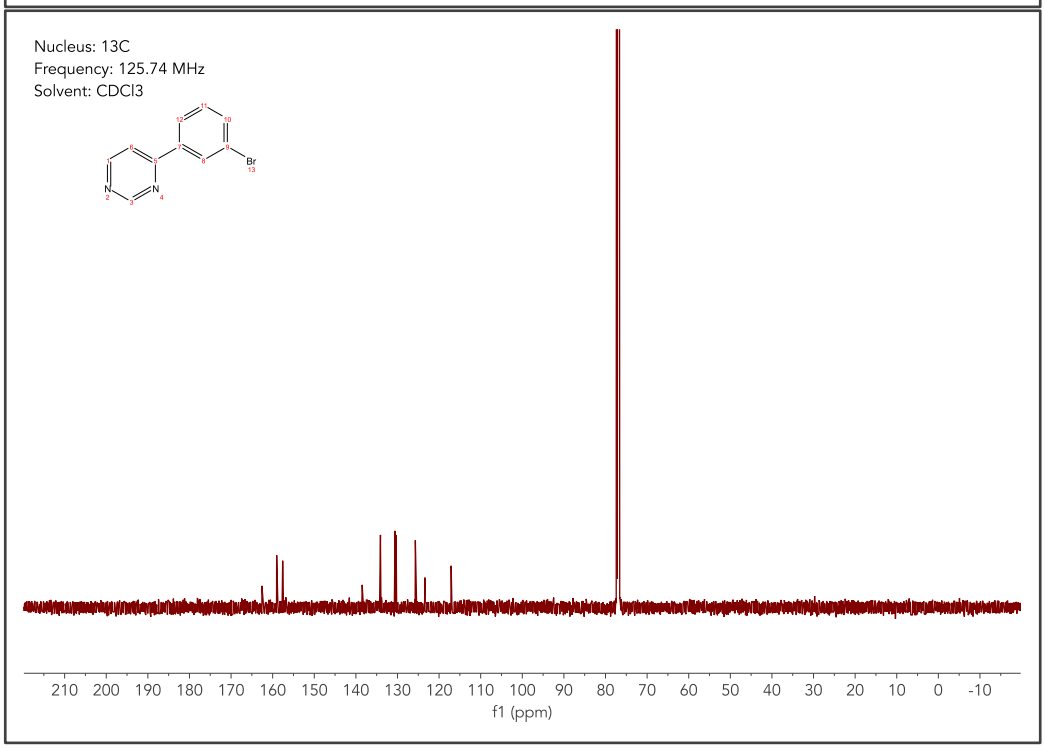

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
0.99
1.03
2.03
1.00
1.02
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

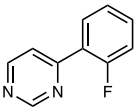
Compound **S9**

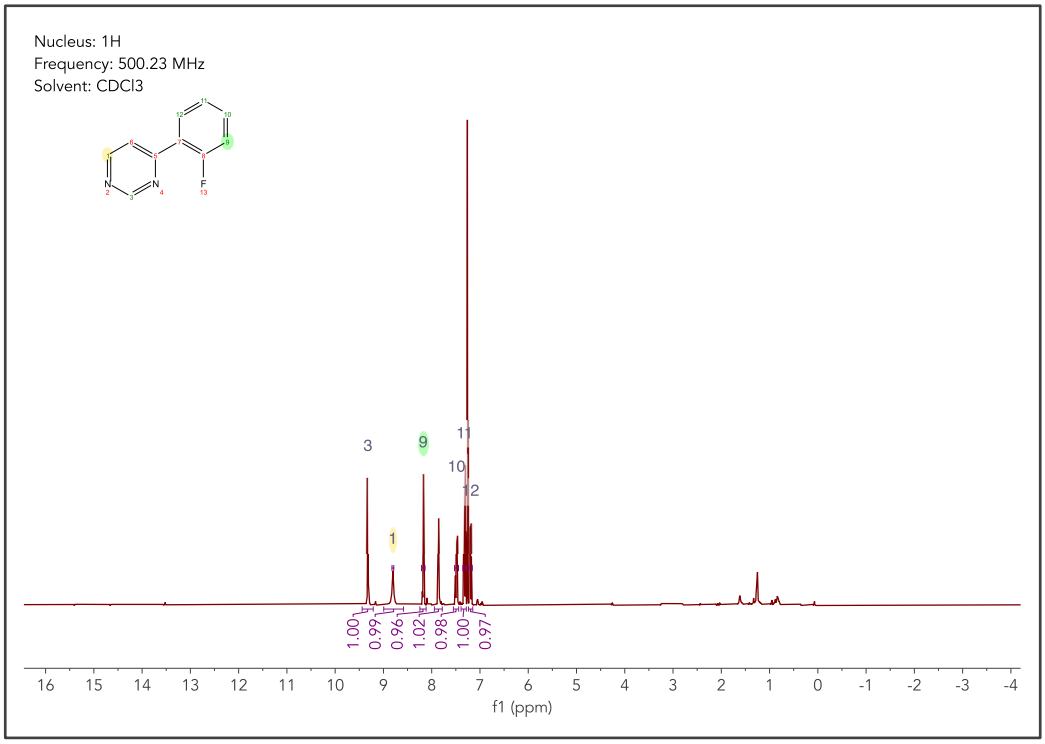

Br
N
N


Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
Br
N
N
1.02
1.05
1.02
1.03
1.02
1.00
1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

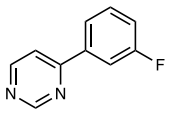

Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
Br
N
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

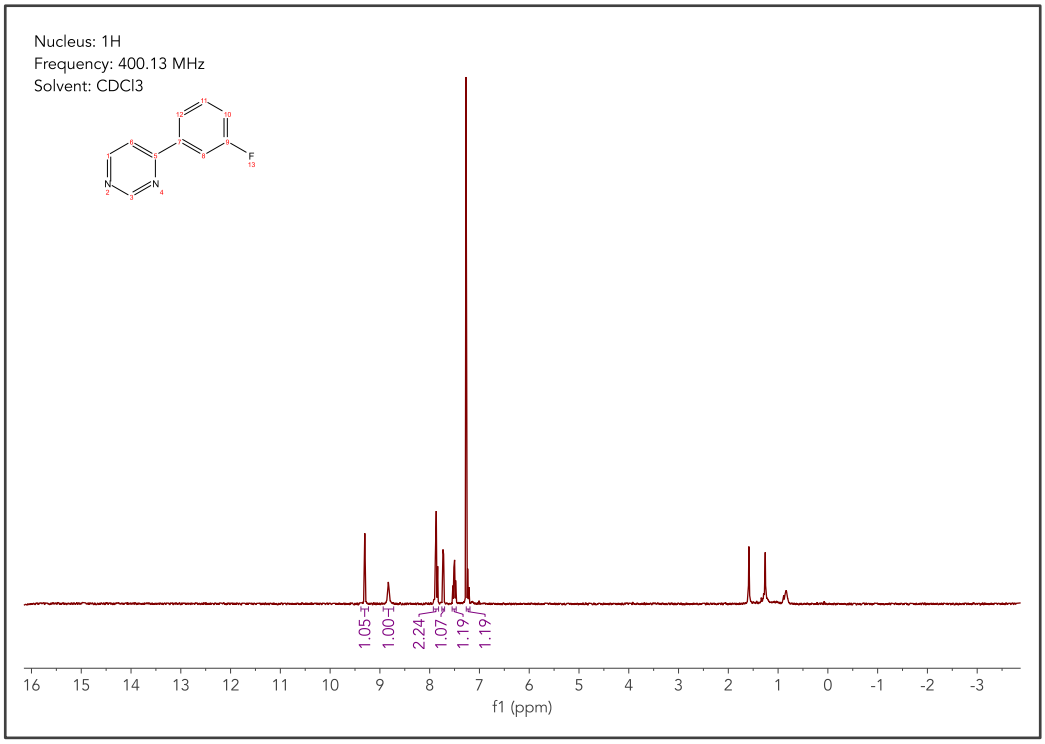
Compound **S10**



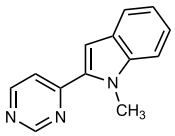


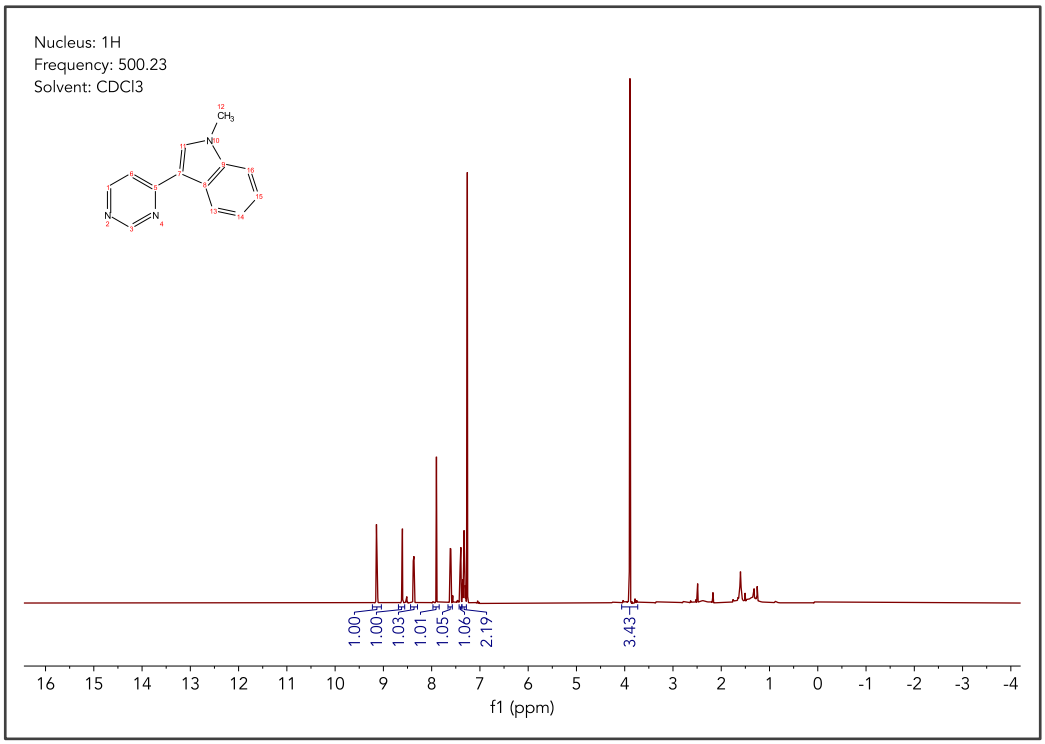
Compound **S11**



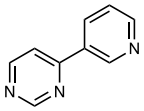


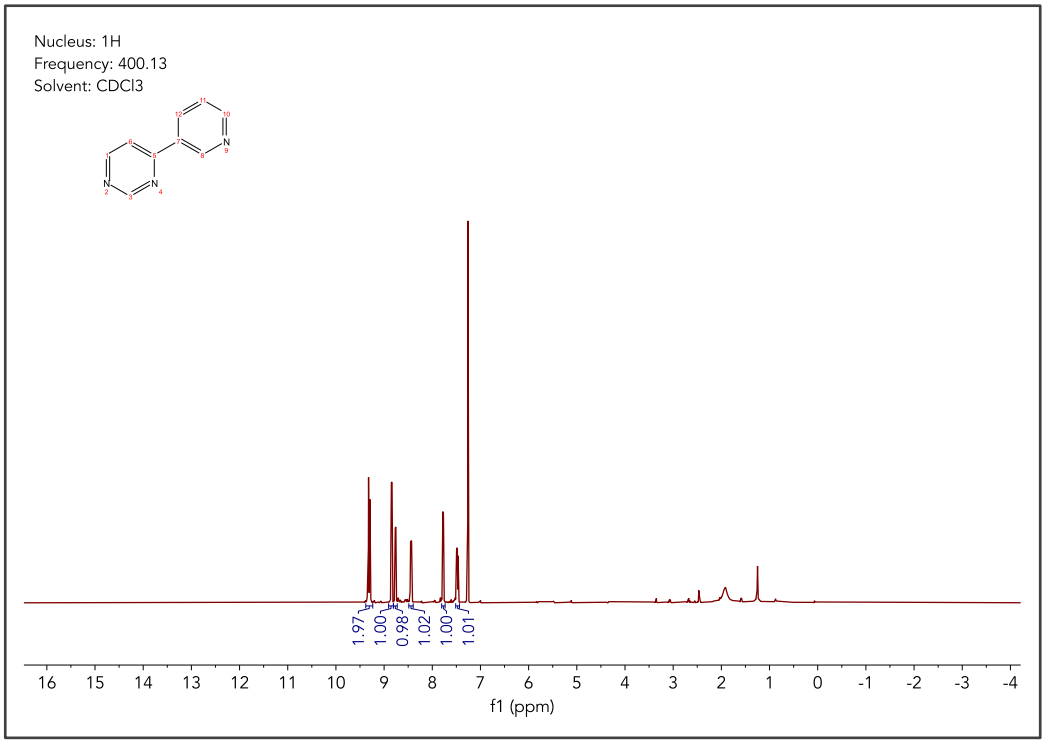
Compound **S12**



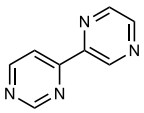


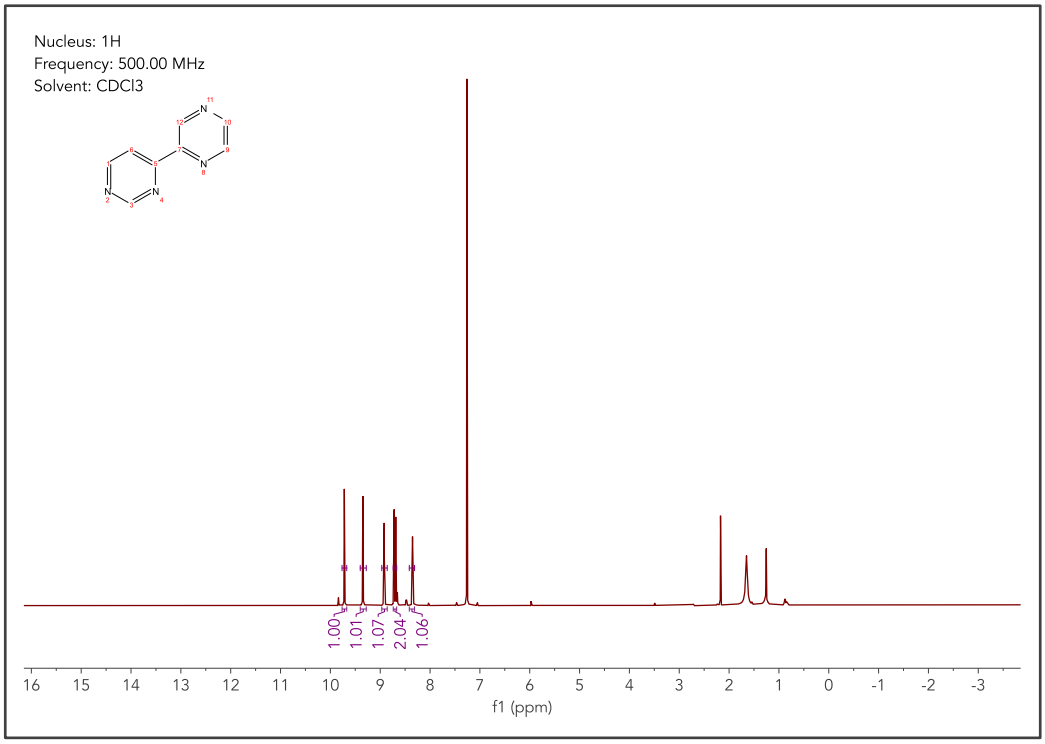
Compound **S13**



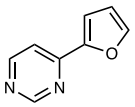


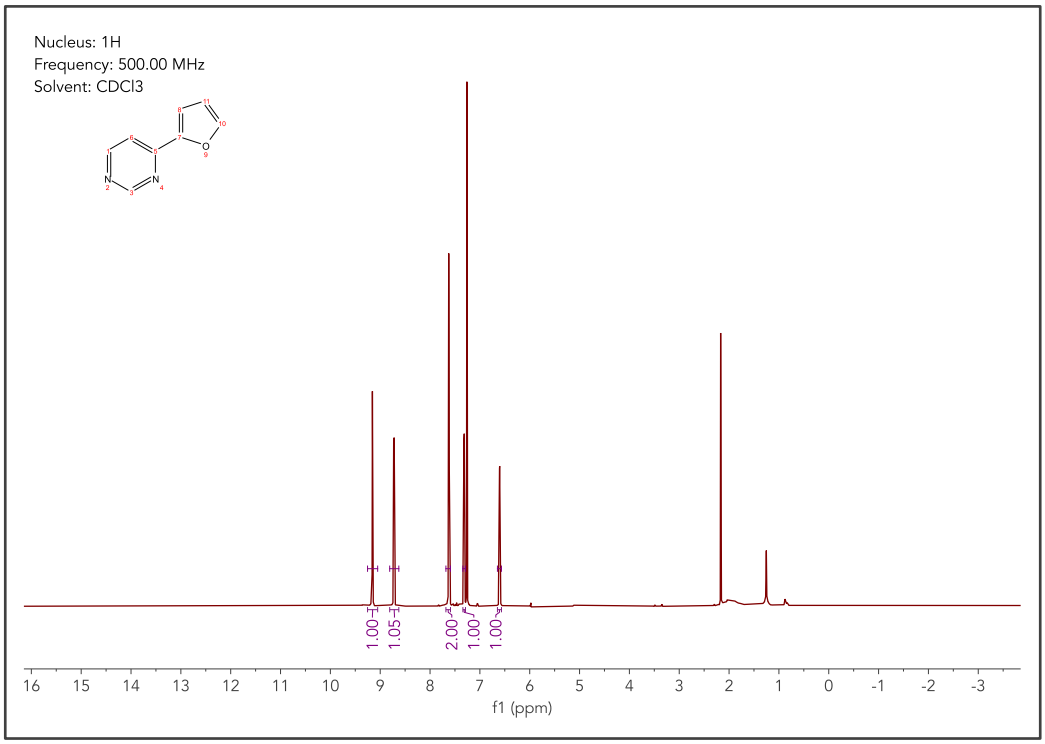
Compound **S14**

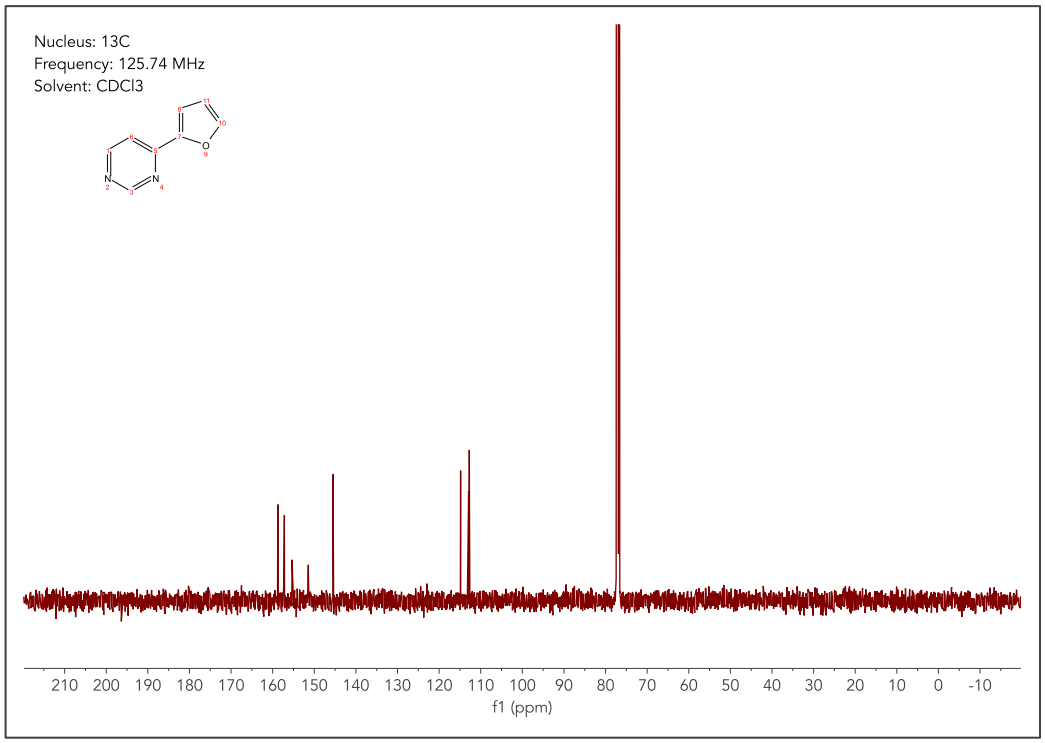




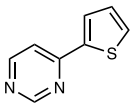
Compound **S15**

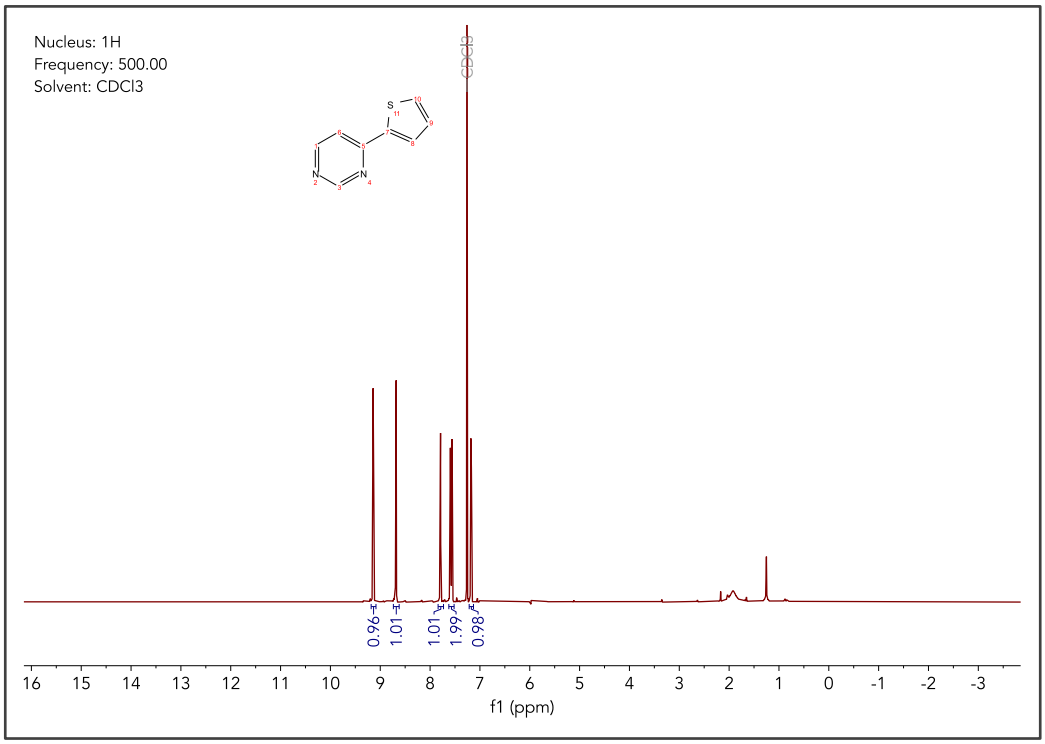




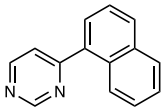


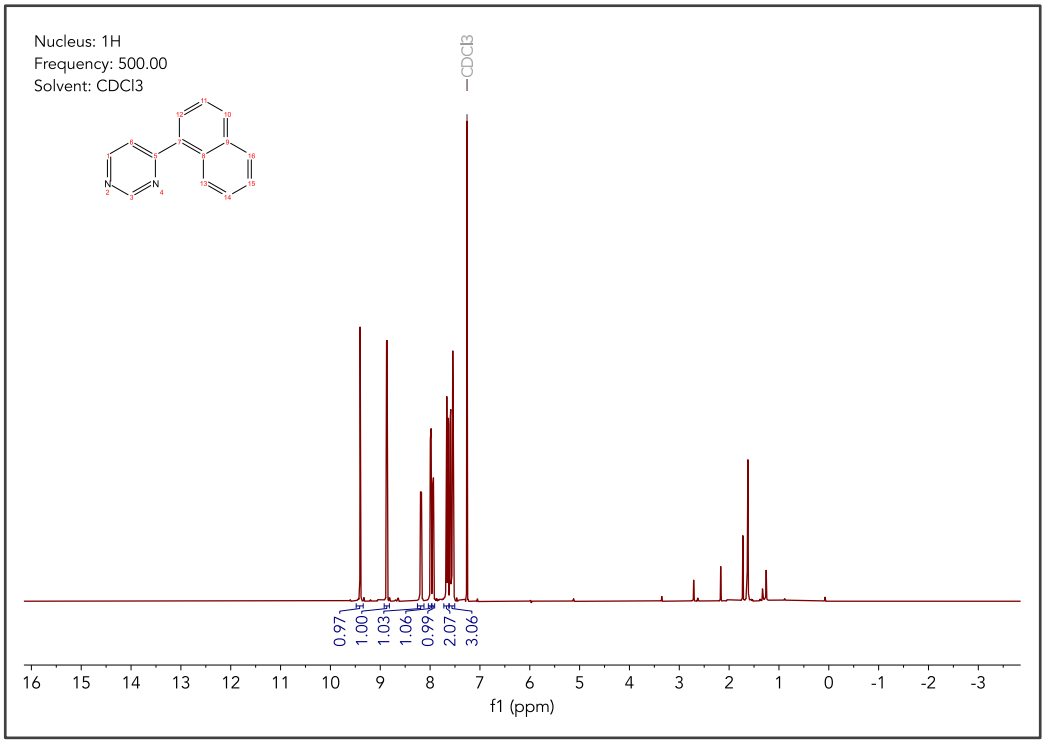
Compound **S16**



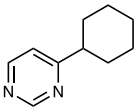


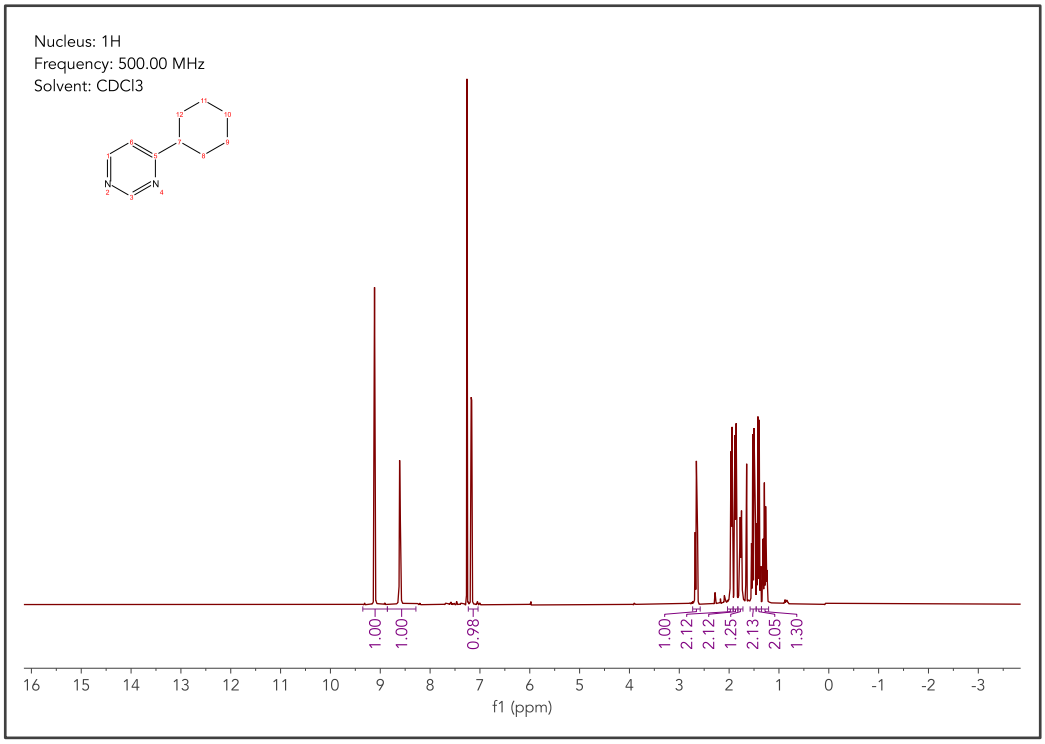
Compound **S17**



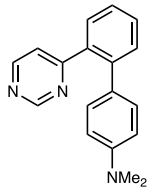


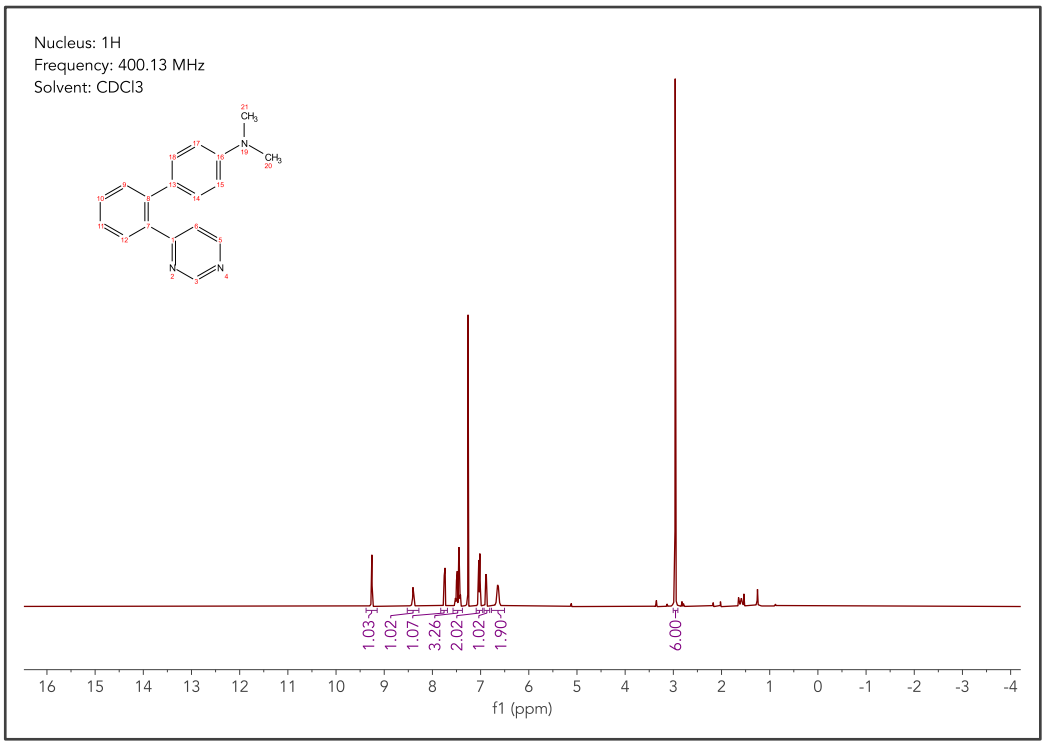
Compound **S18**



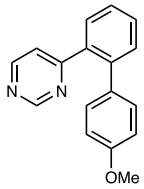


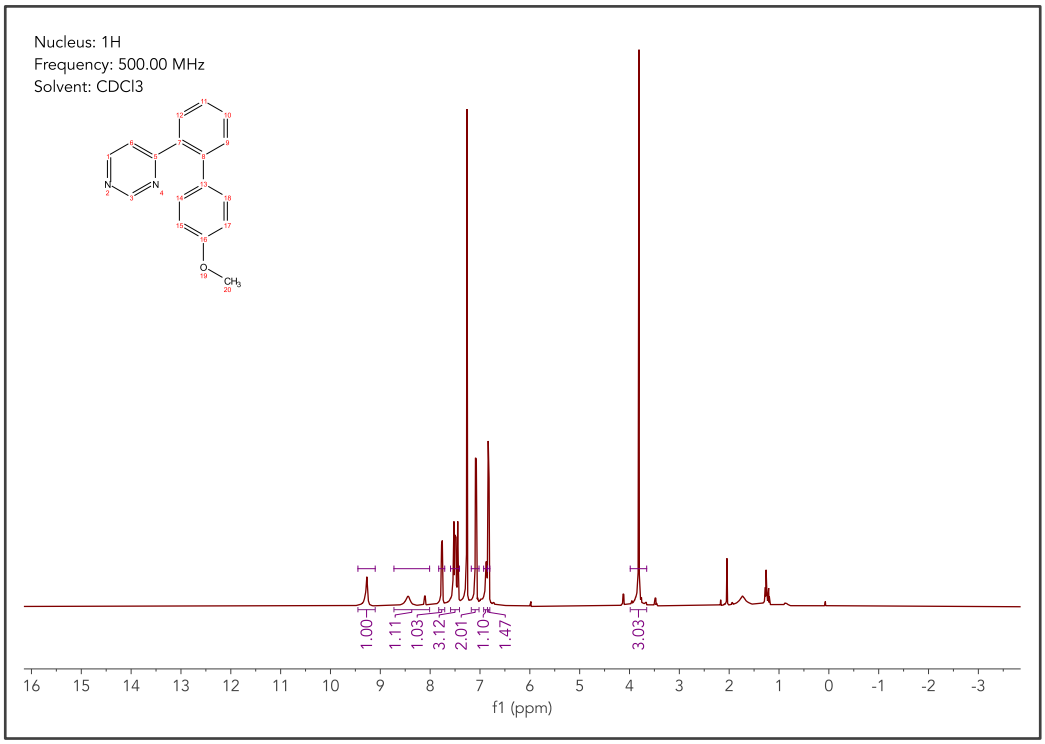
Compound **S19**



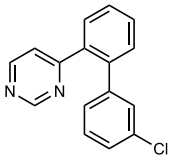


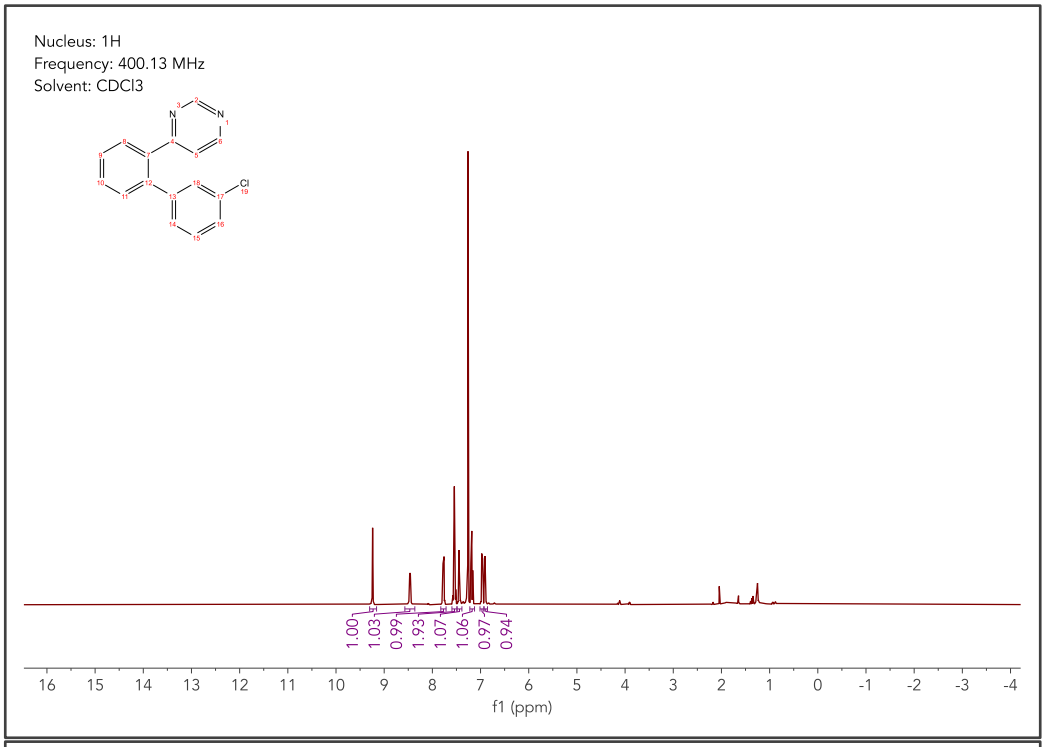
Compound **S20**

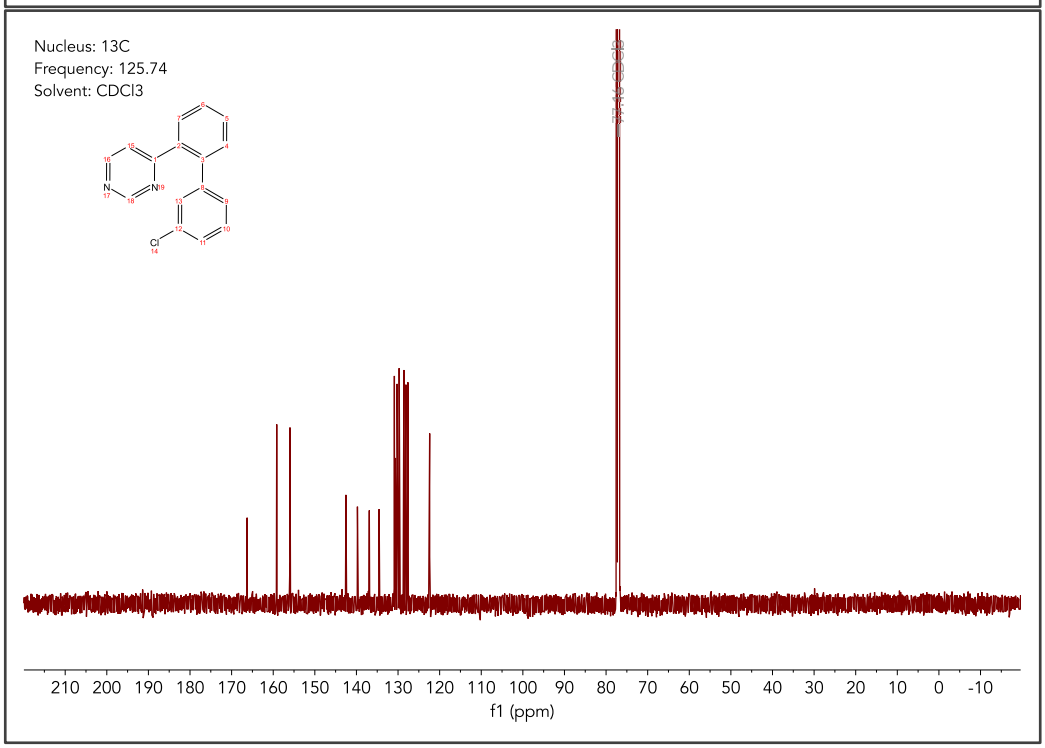




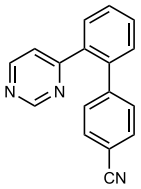
Compound **S21**

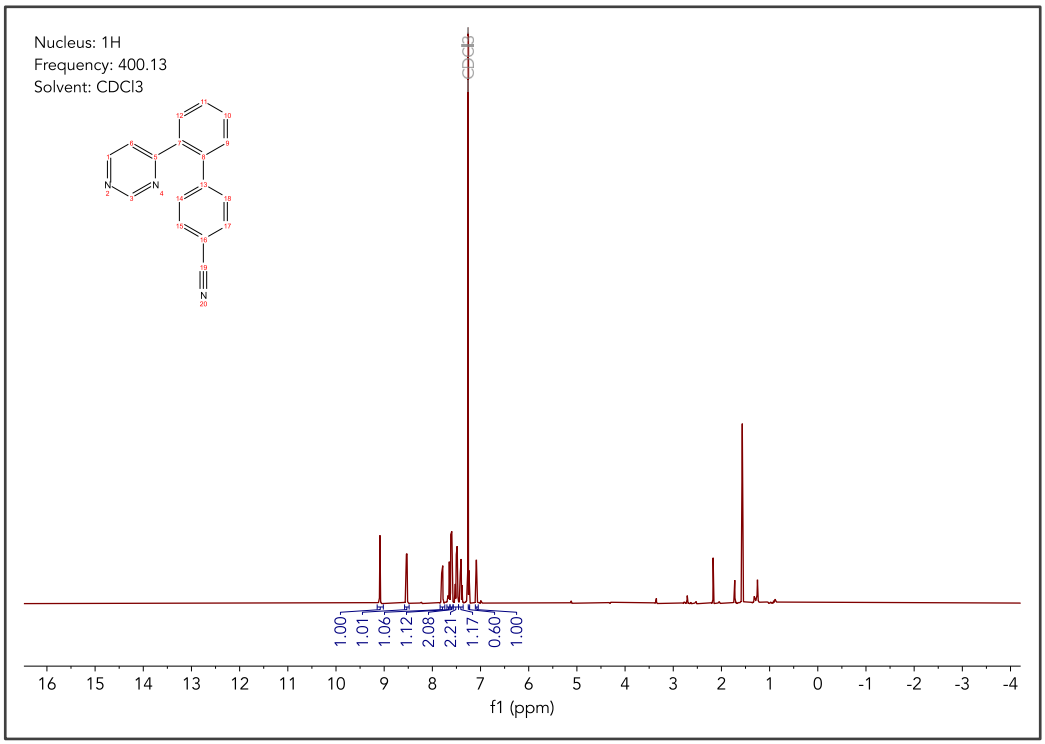




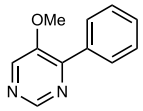


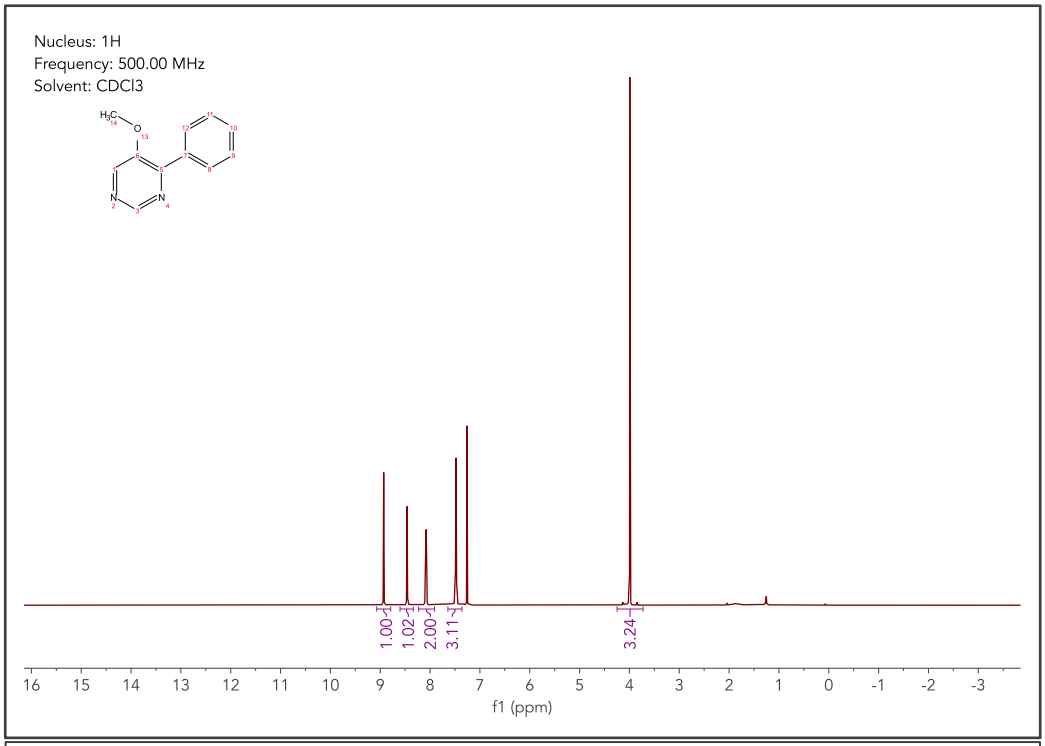
Compound **S22**

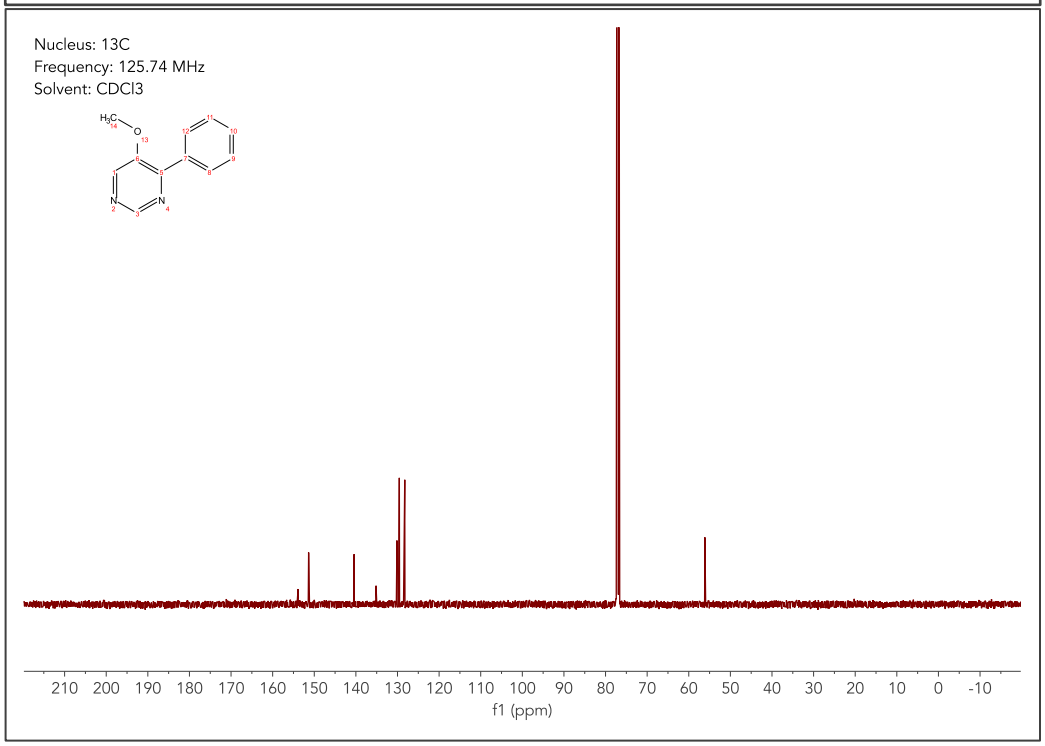




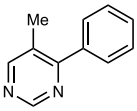
Compound **S23**

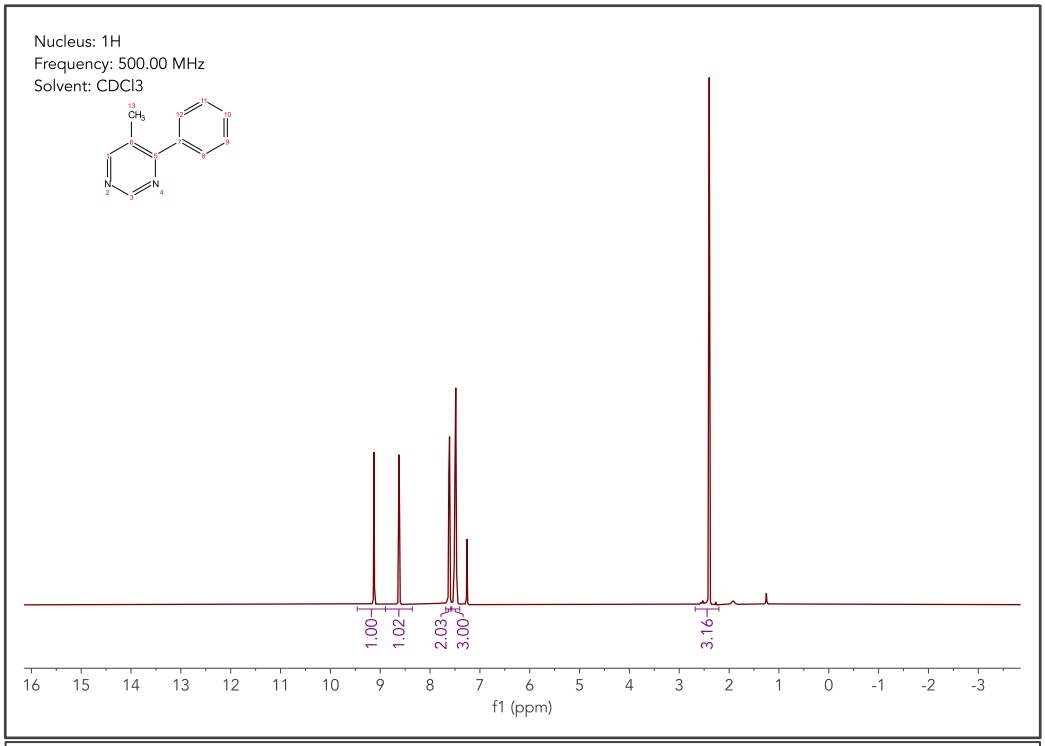


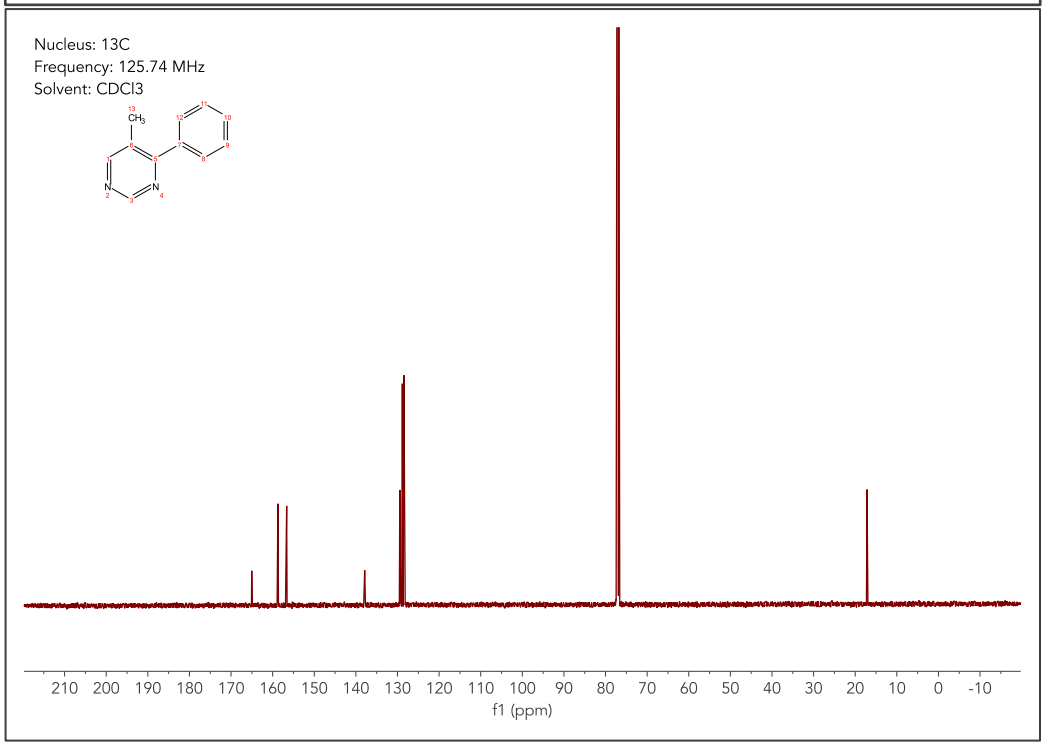




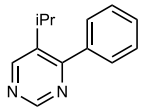
Compound **S24**

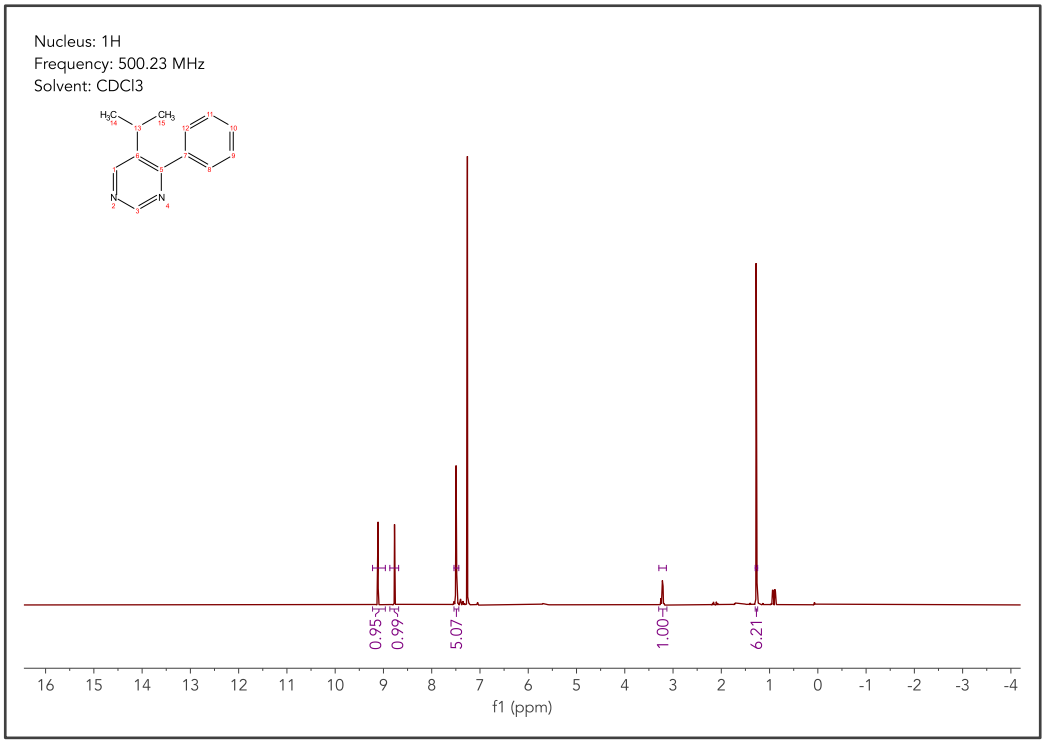




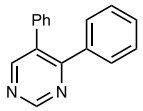


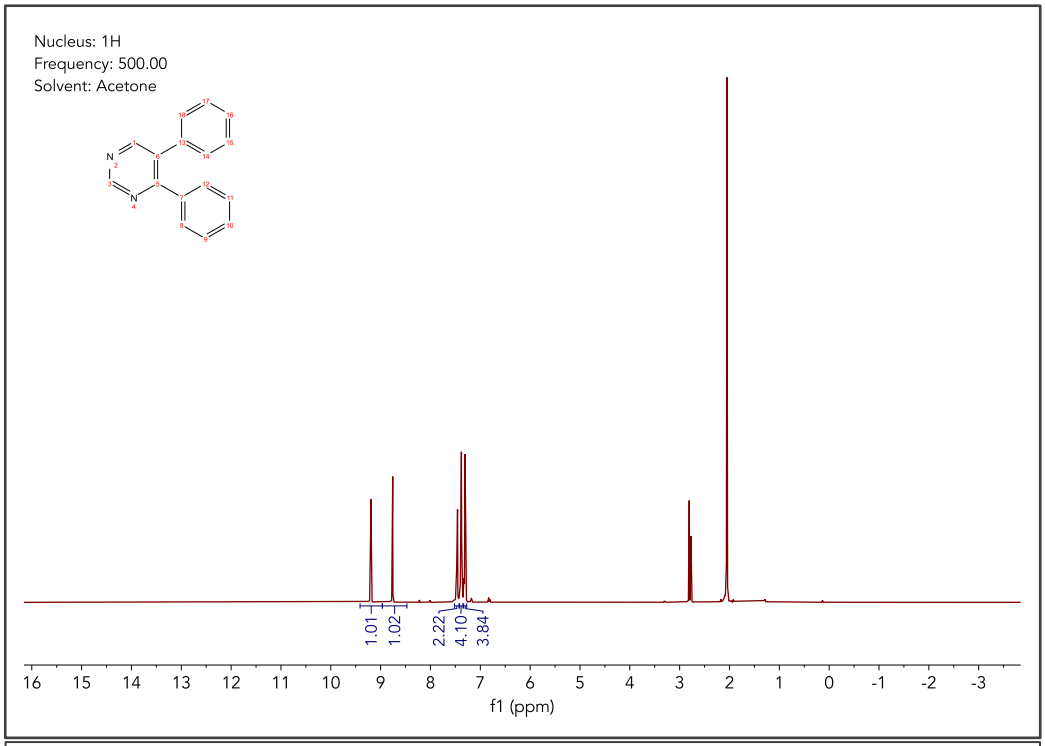
Compound **S25**

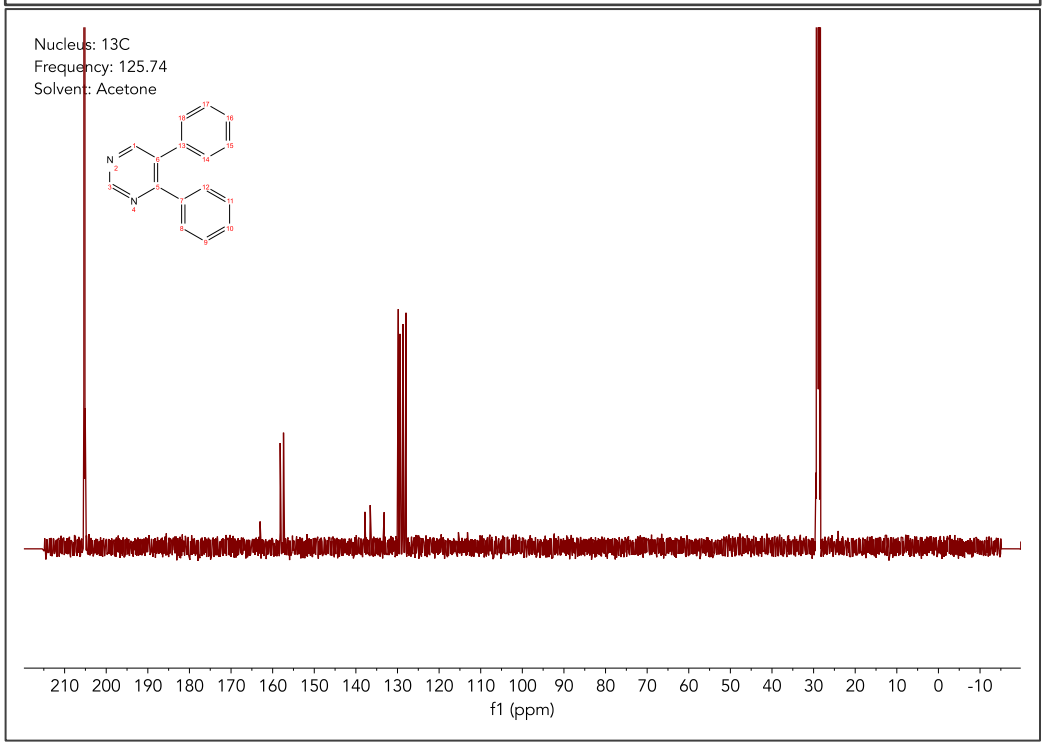




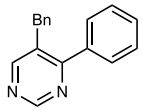
Compound **S26**

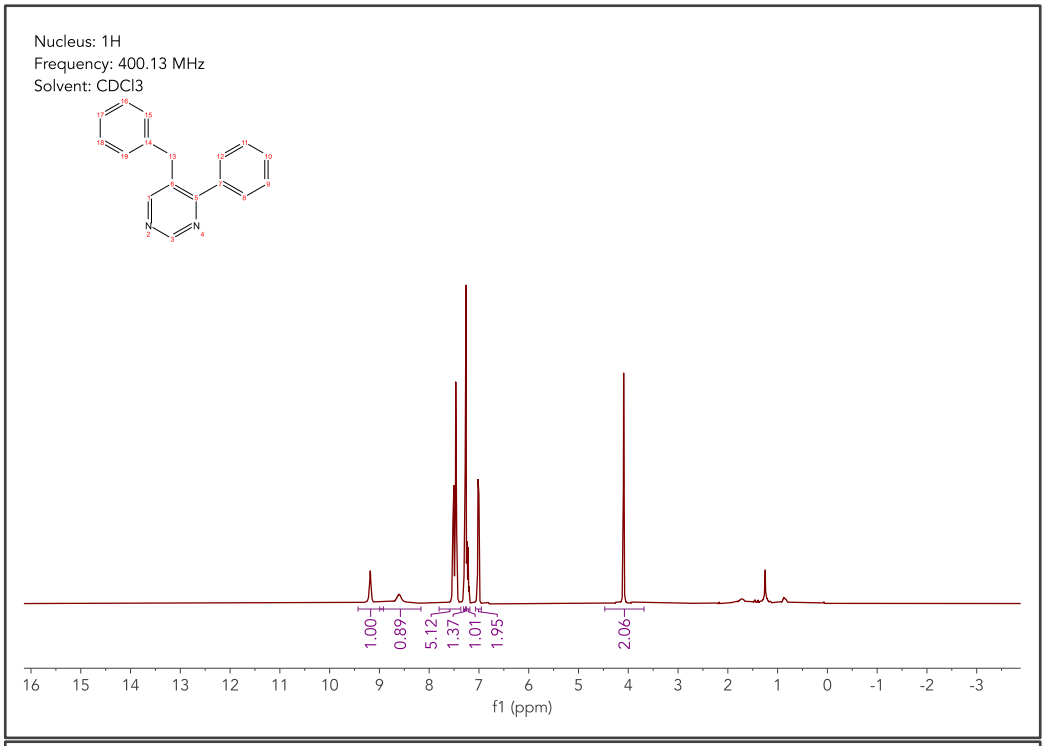


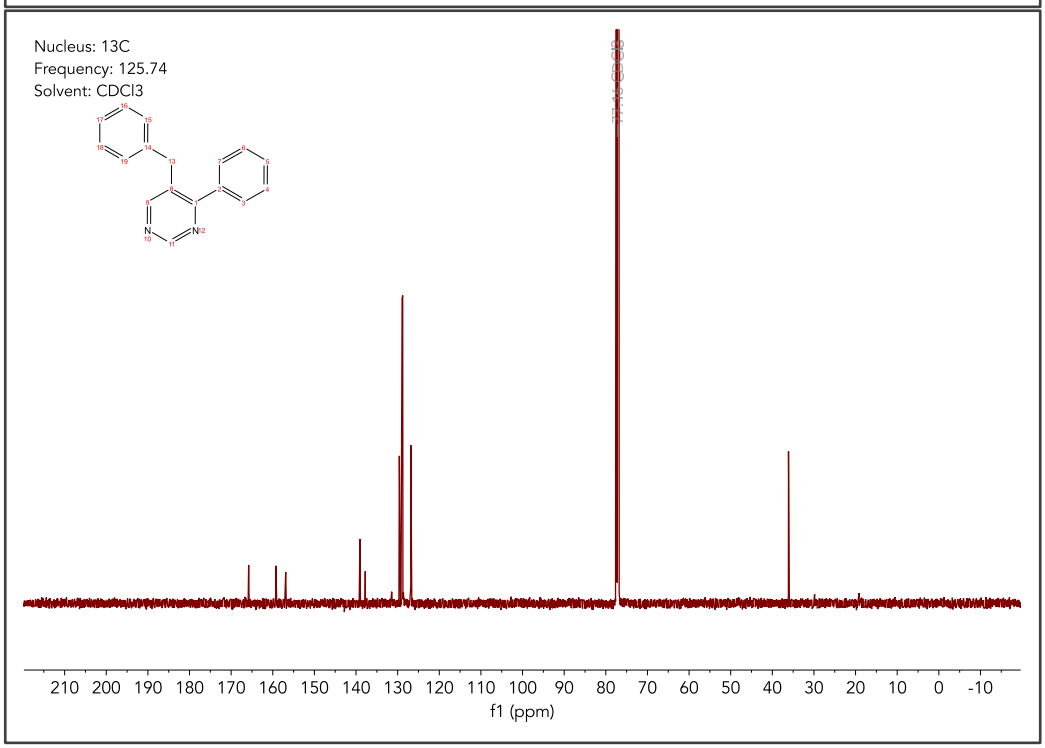




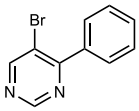
Compound **S27**

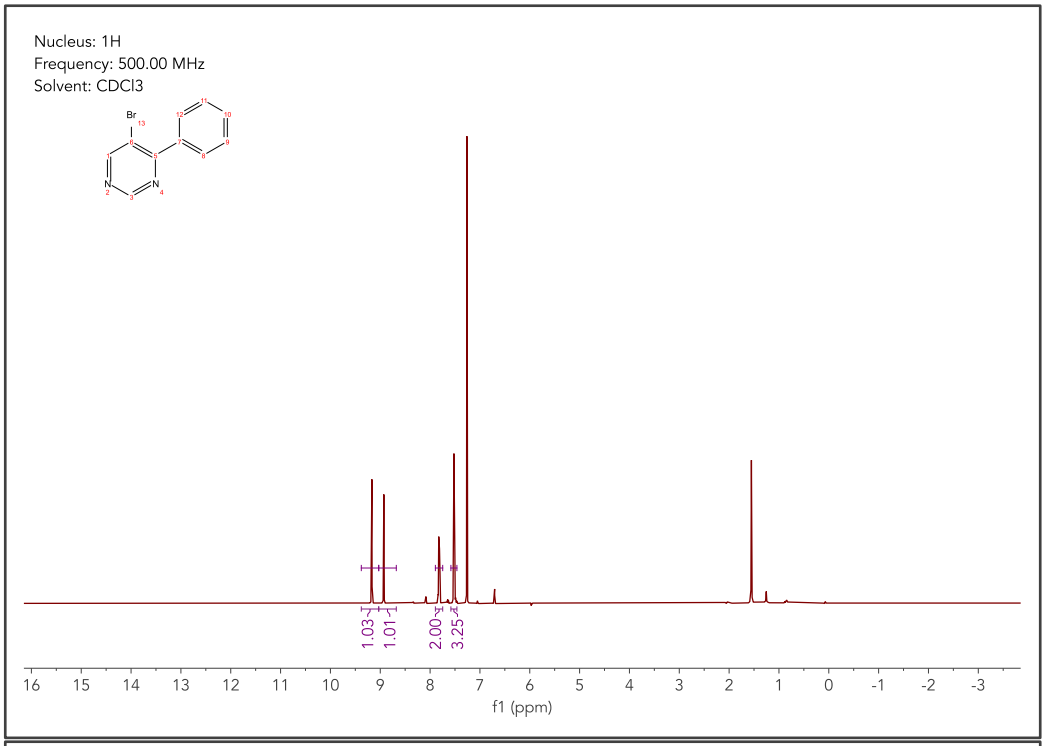


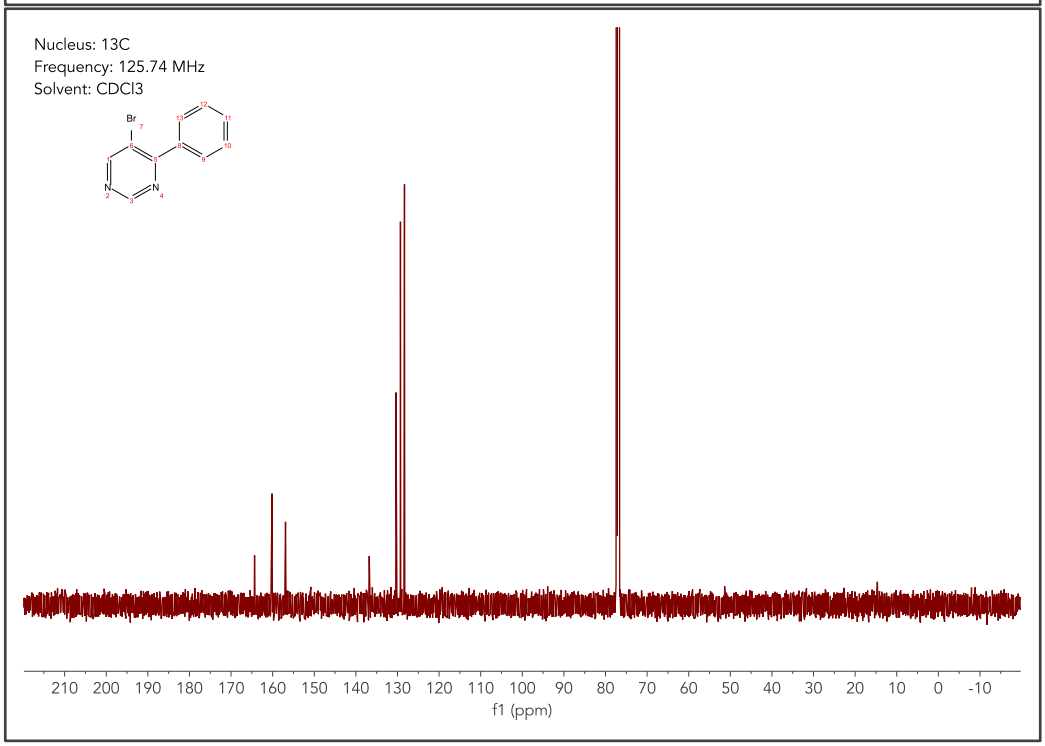




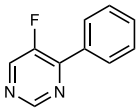
Compound **S28**

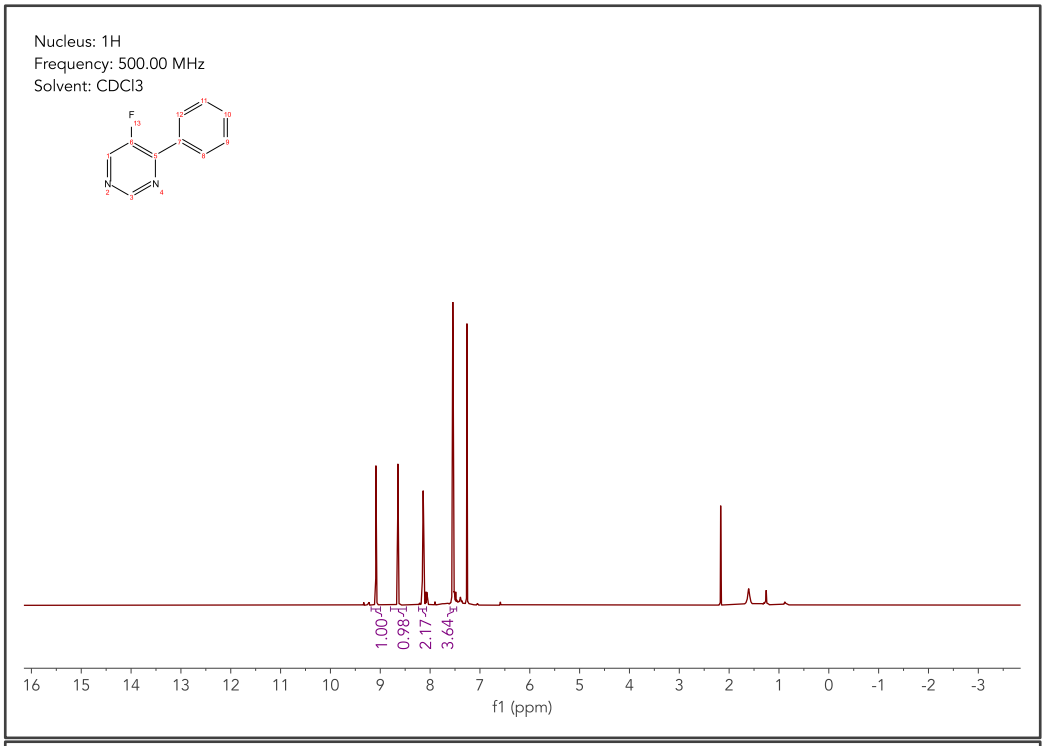


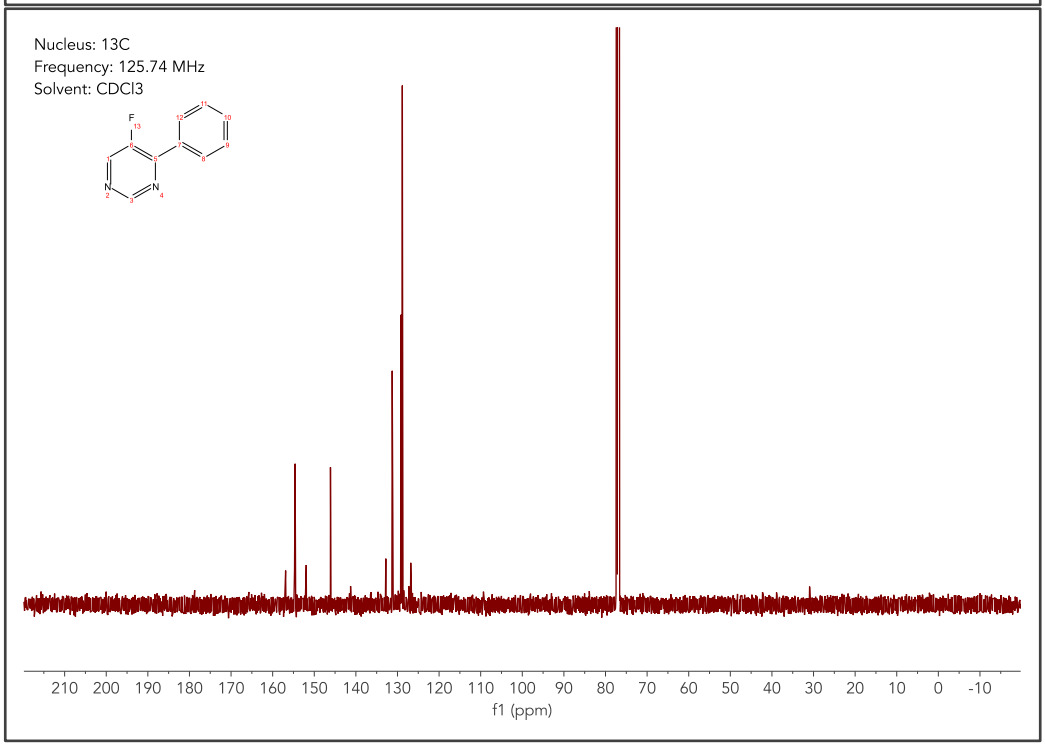




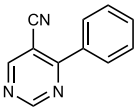
Compound **S29**

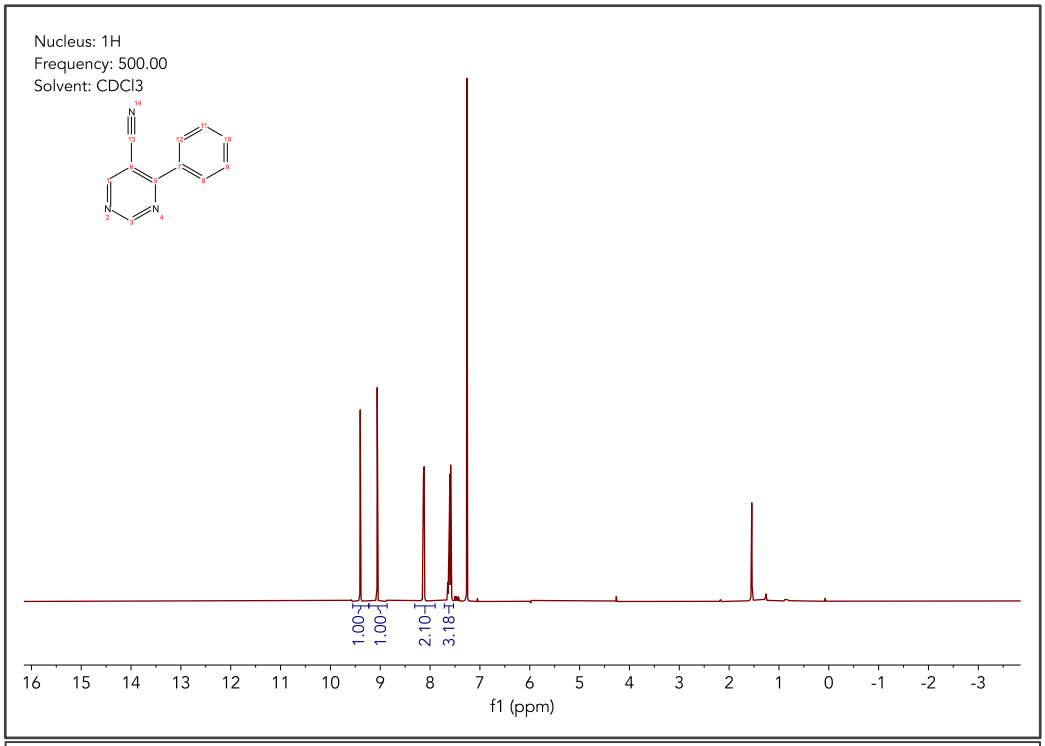


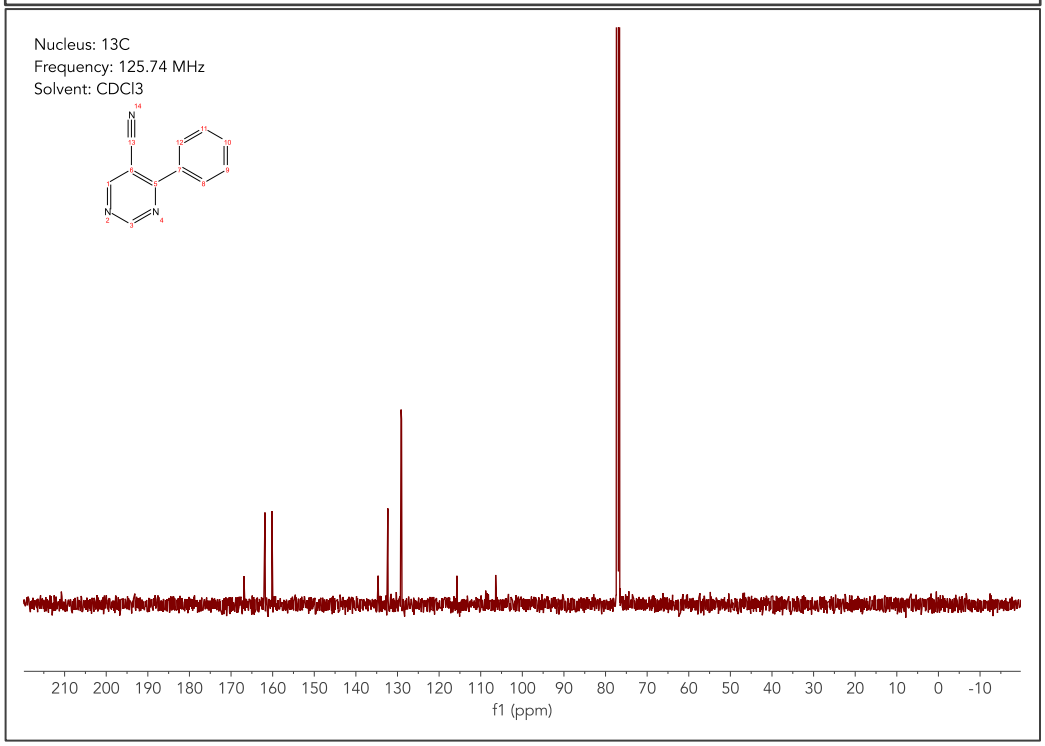




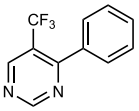
Compound **S30**

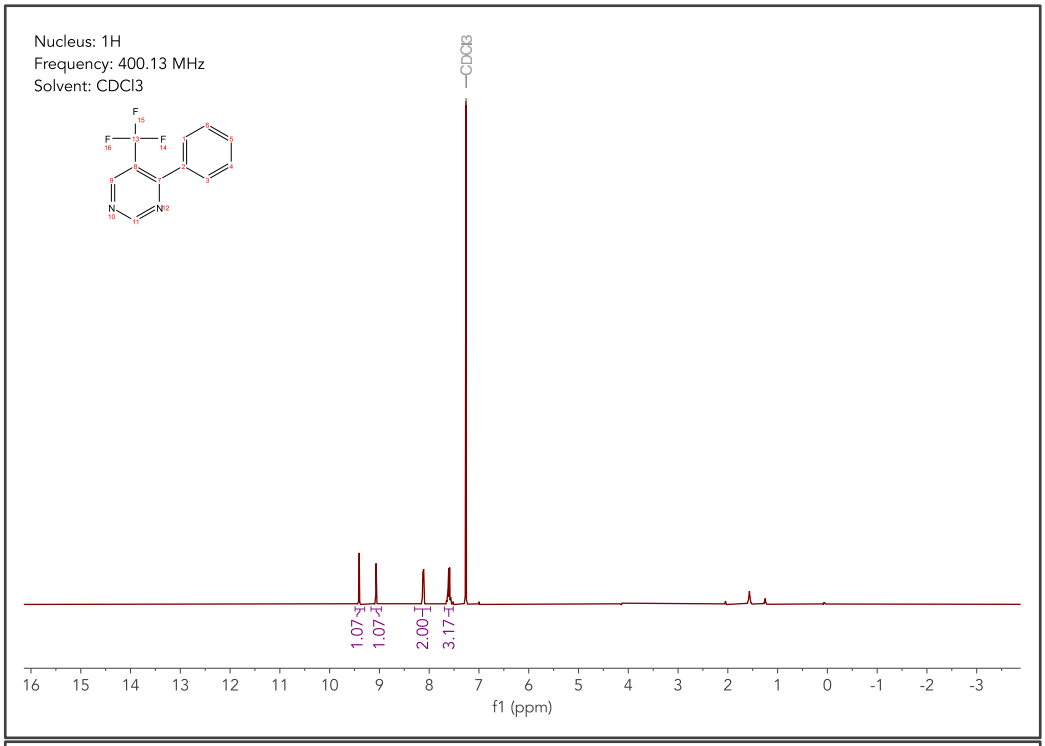


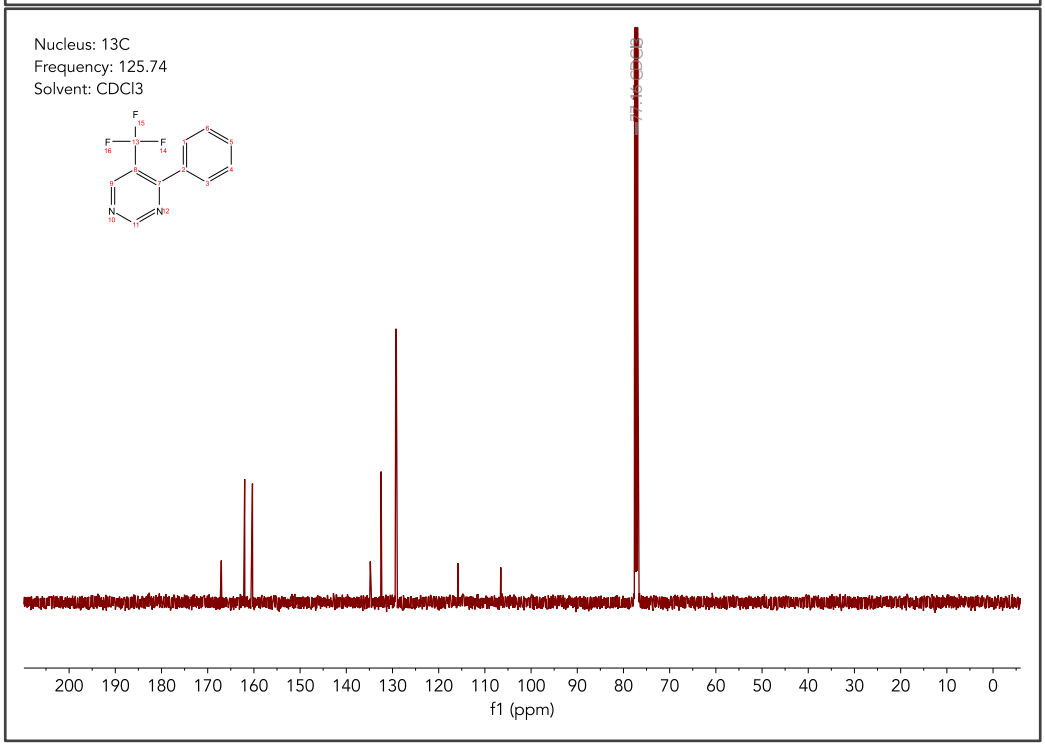




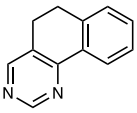
Compound **S31**

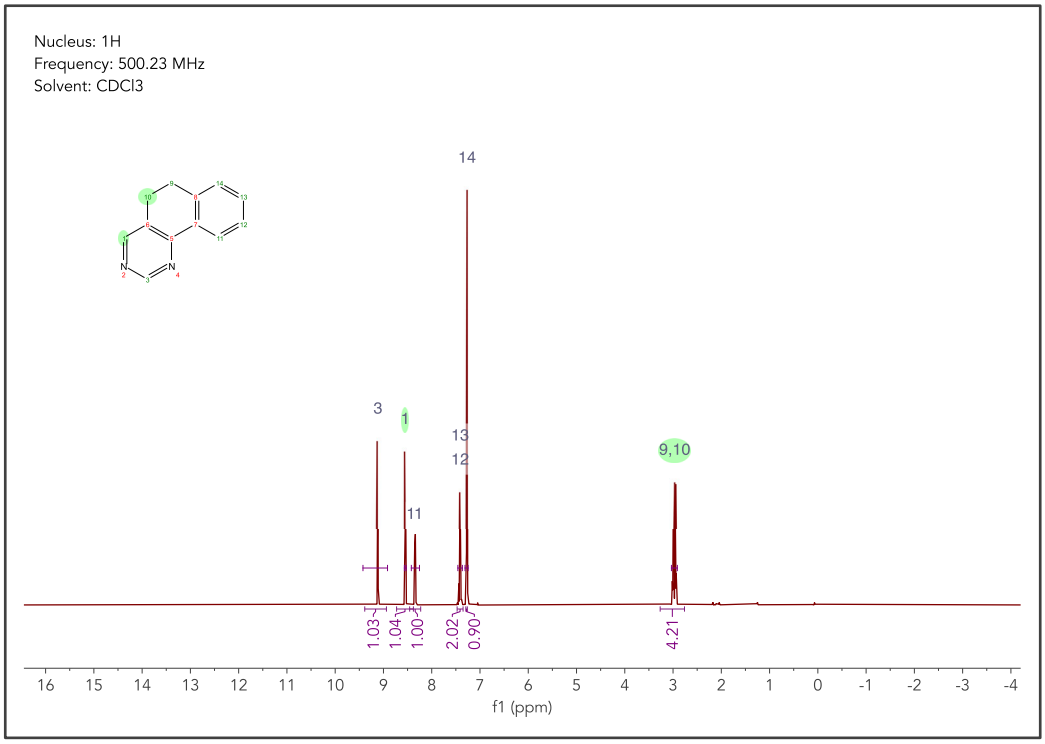




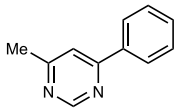


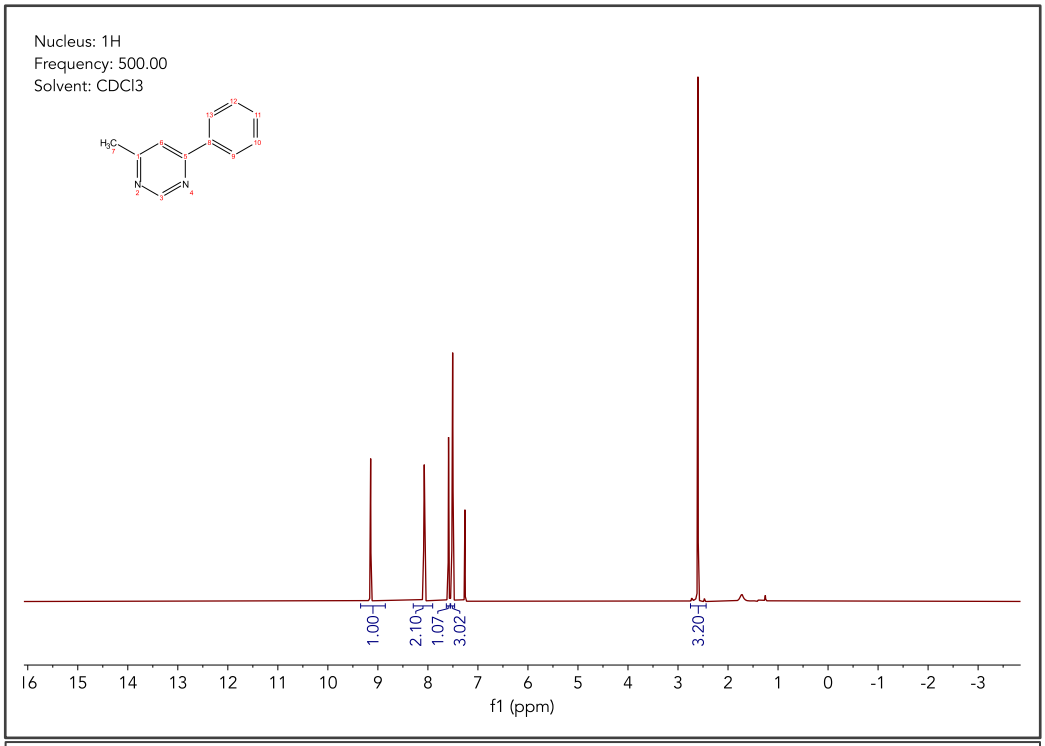
Compound **S32**

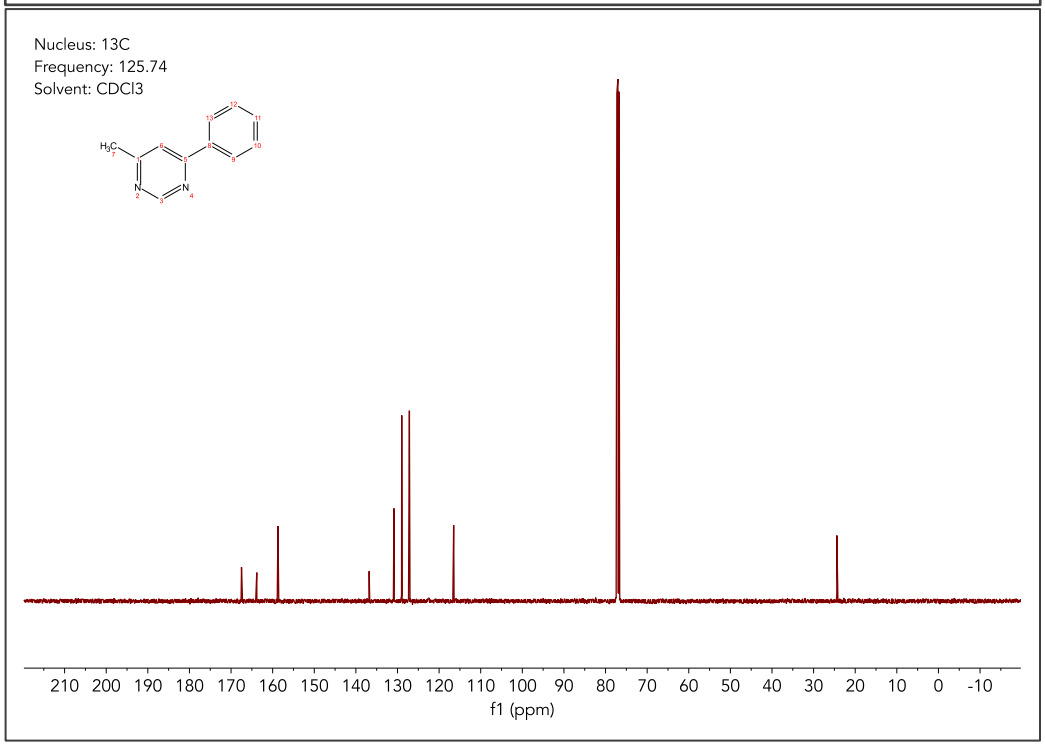




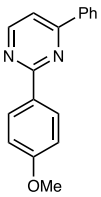
Compound **S33**

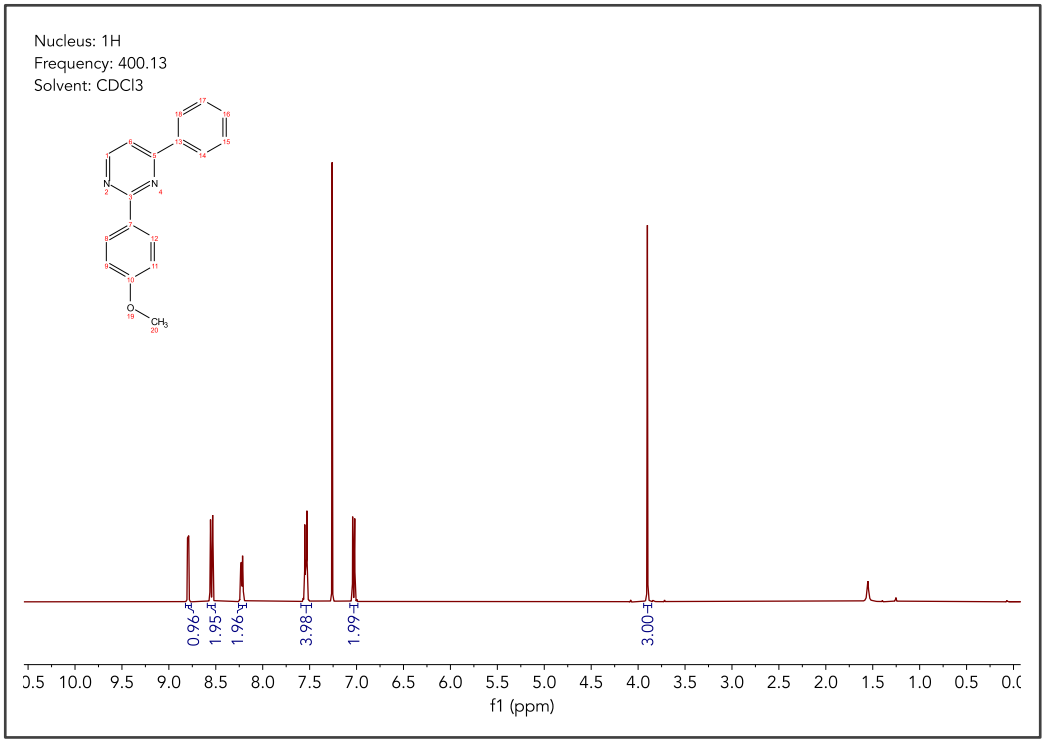




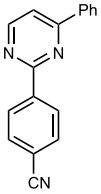


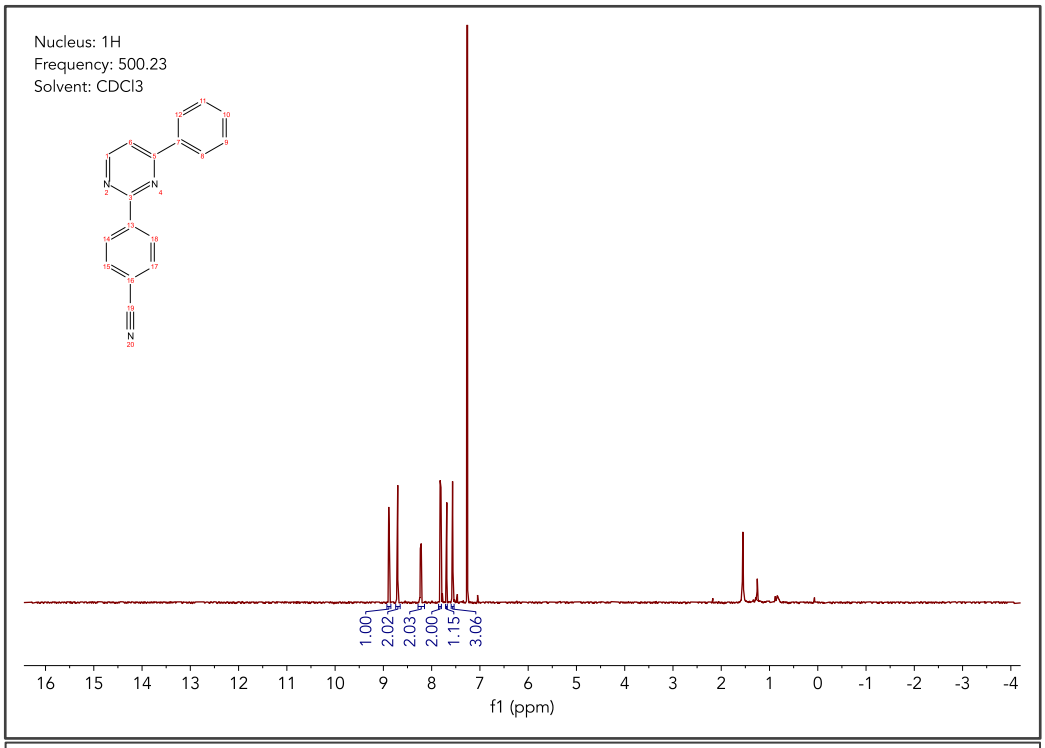
Compound **S34**

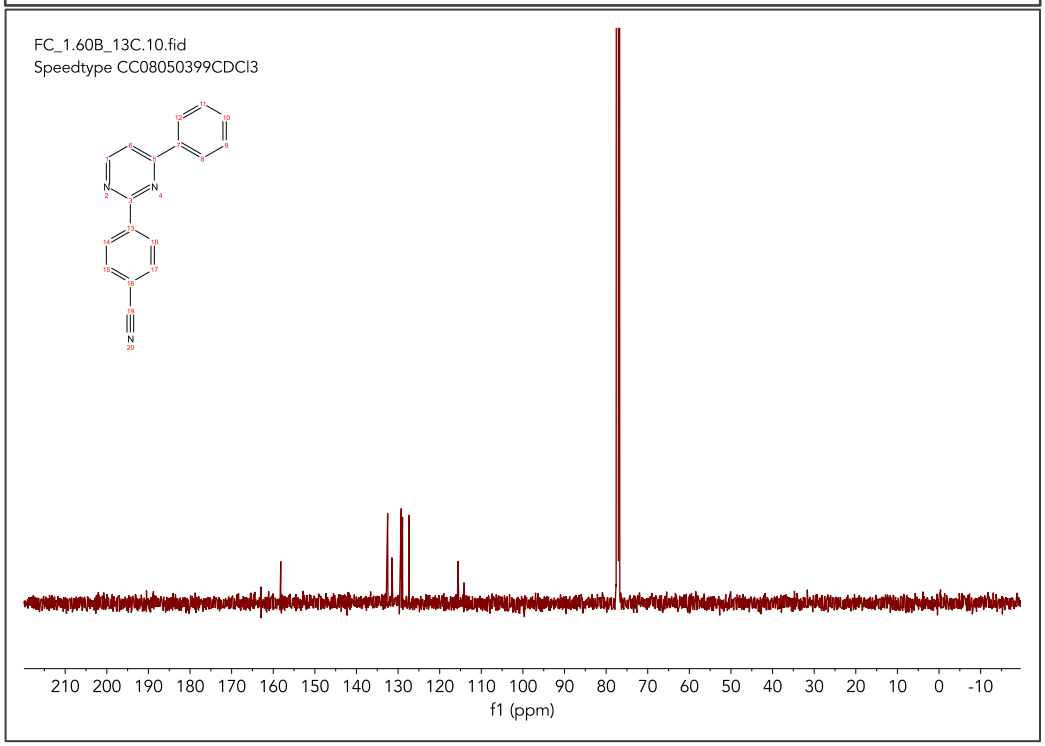




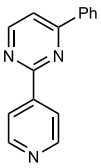
Compound **S36**

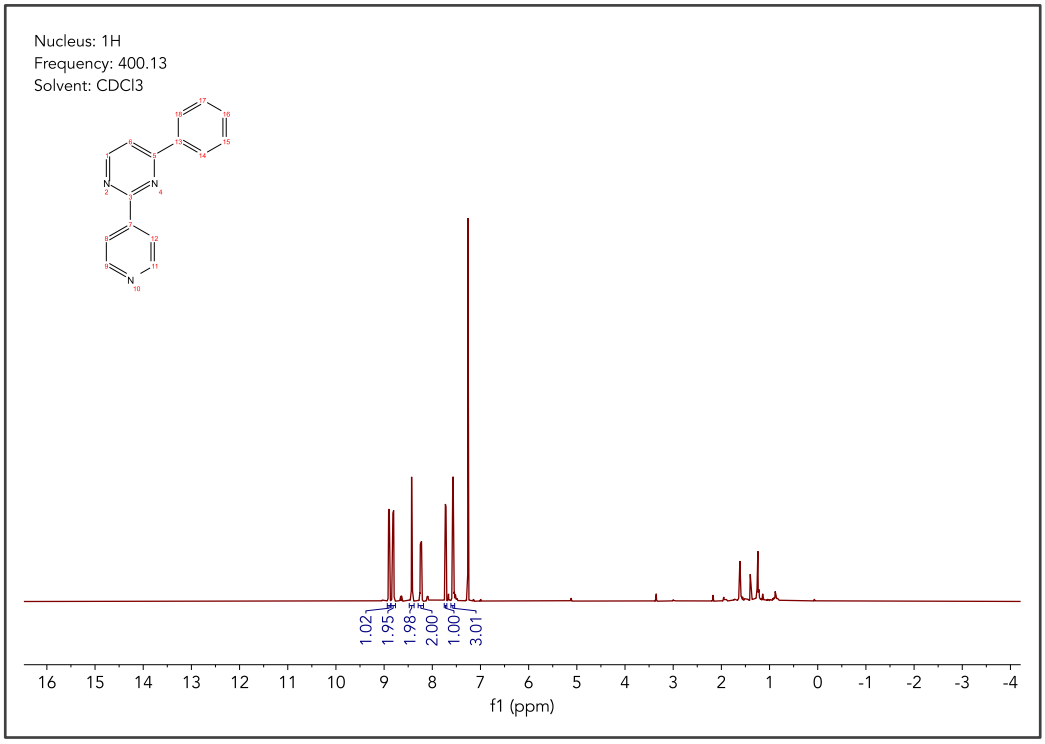




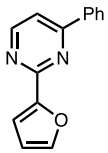


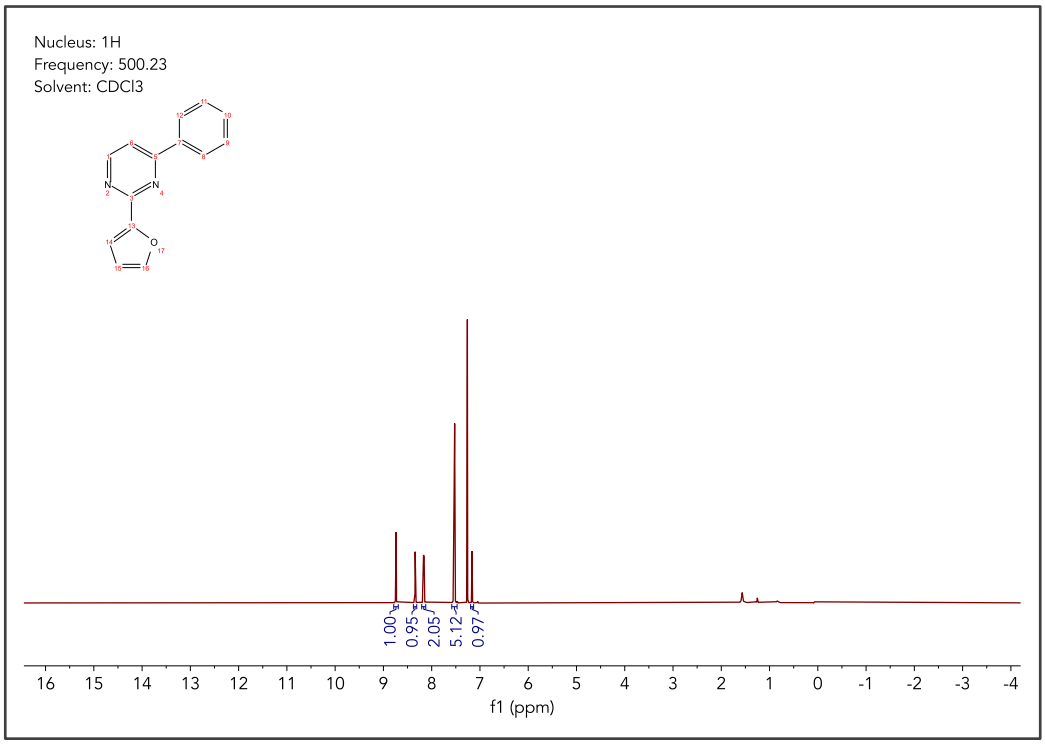
Compound **S37**



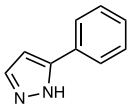


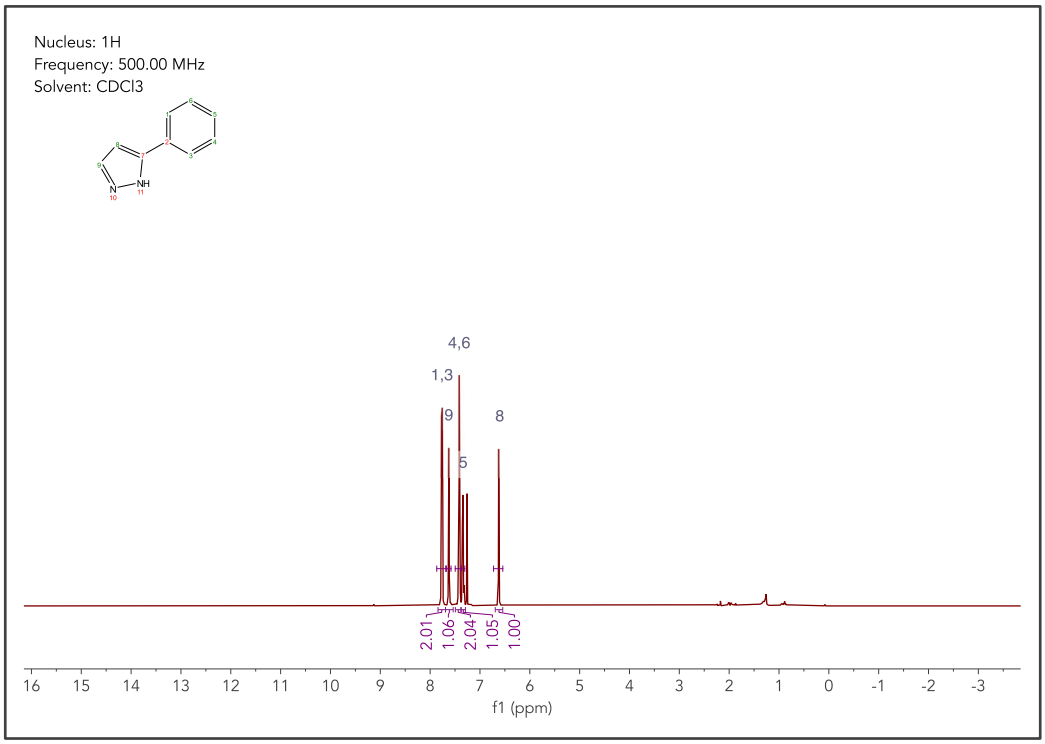
Compound **S38**



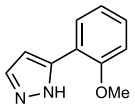


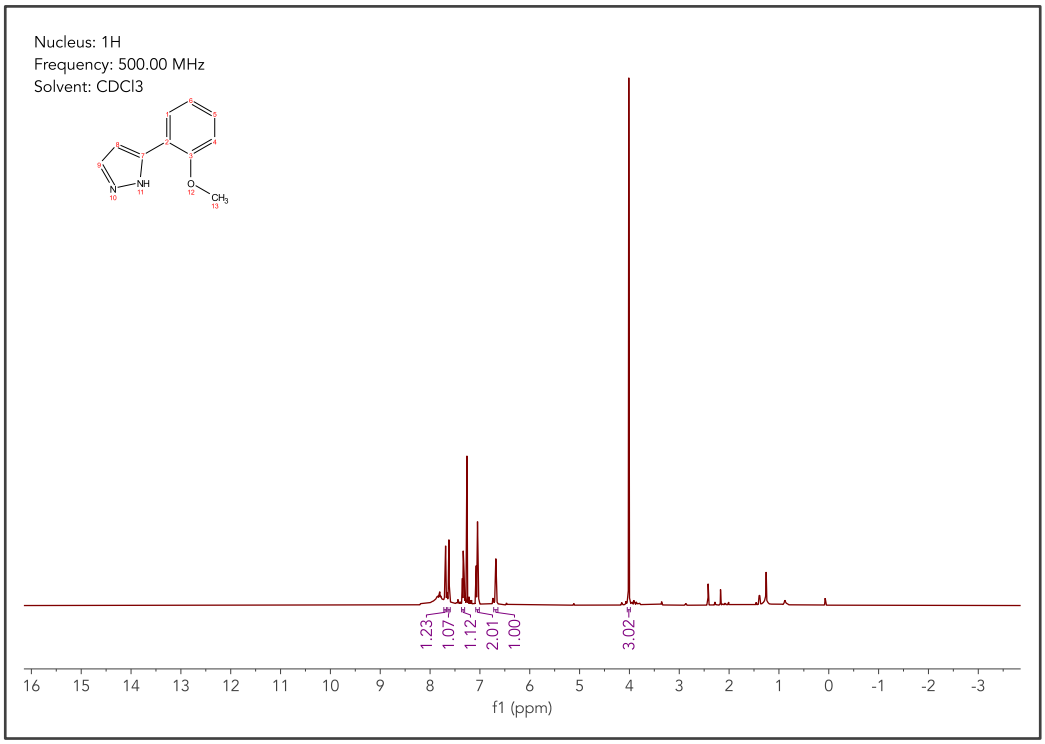
Compound **1**


N
NH

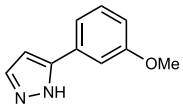

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
4,6
1,3
9
8
5
2.01
1.06
2.04
1.05
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

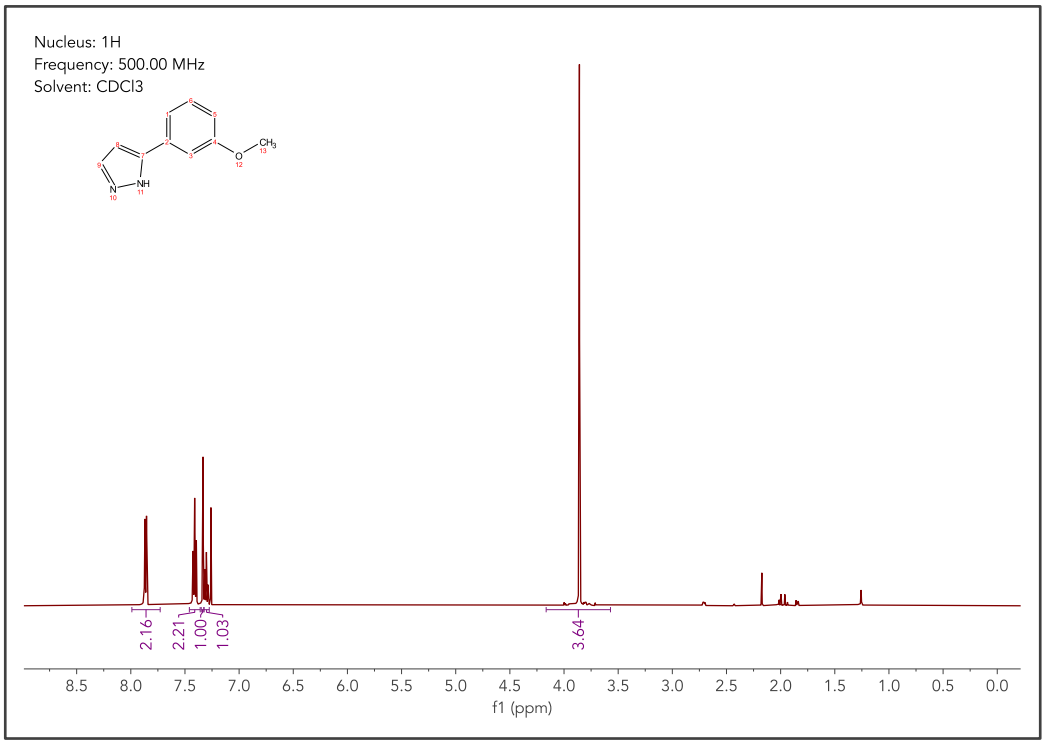
Compound **2a**

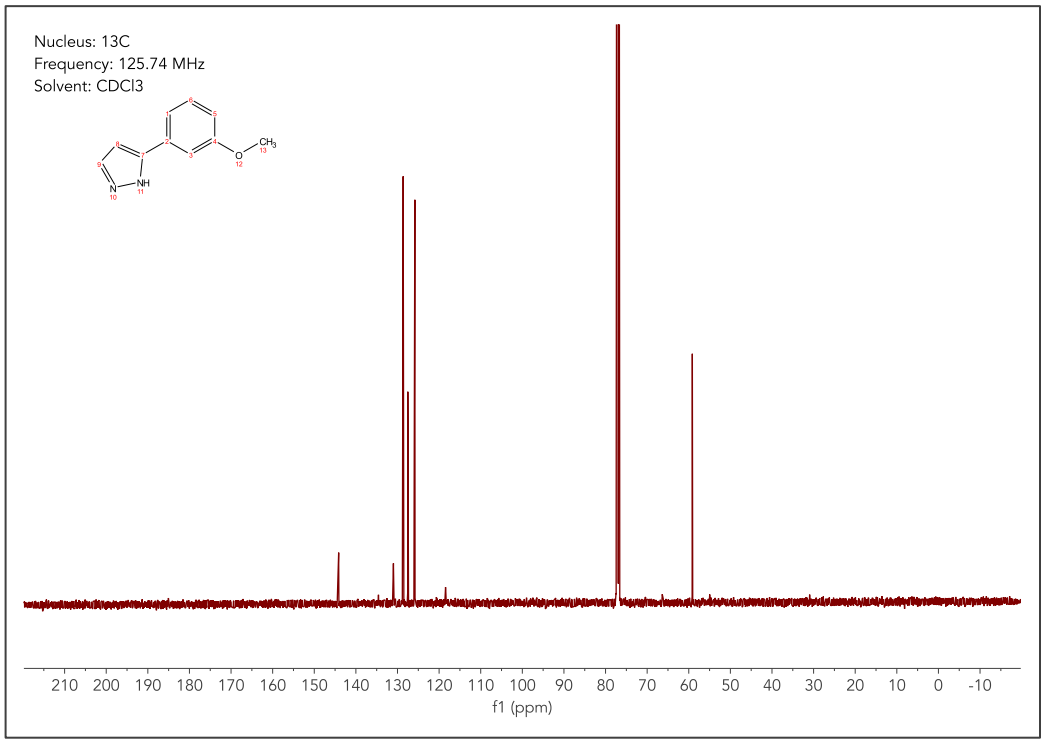

NH
N
OMe


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.23
1.07
1.12
2.01
1.00
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

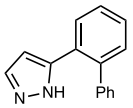
Compound **2b**

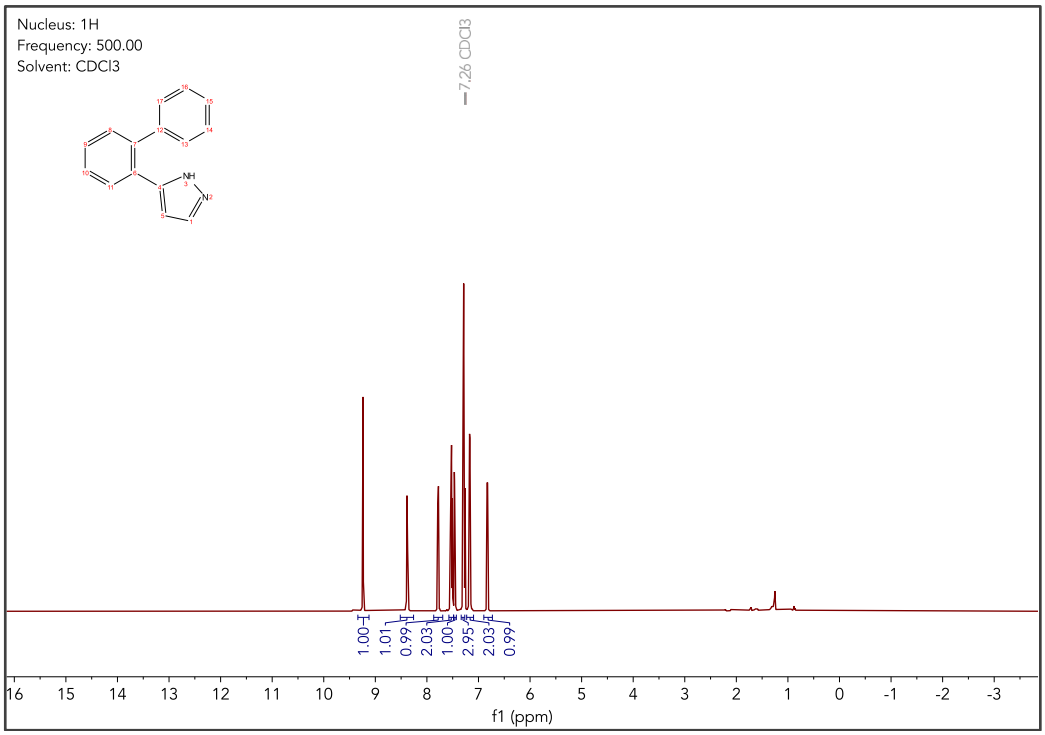

OMe
NH
N

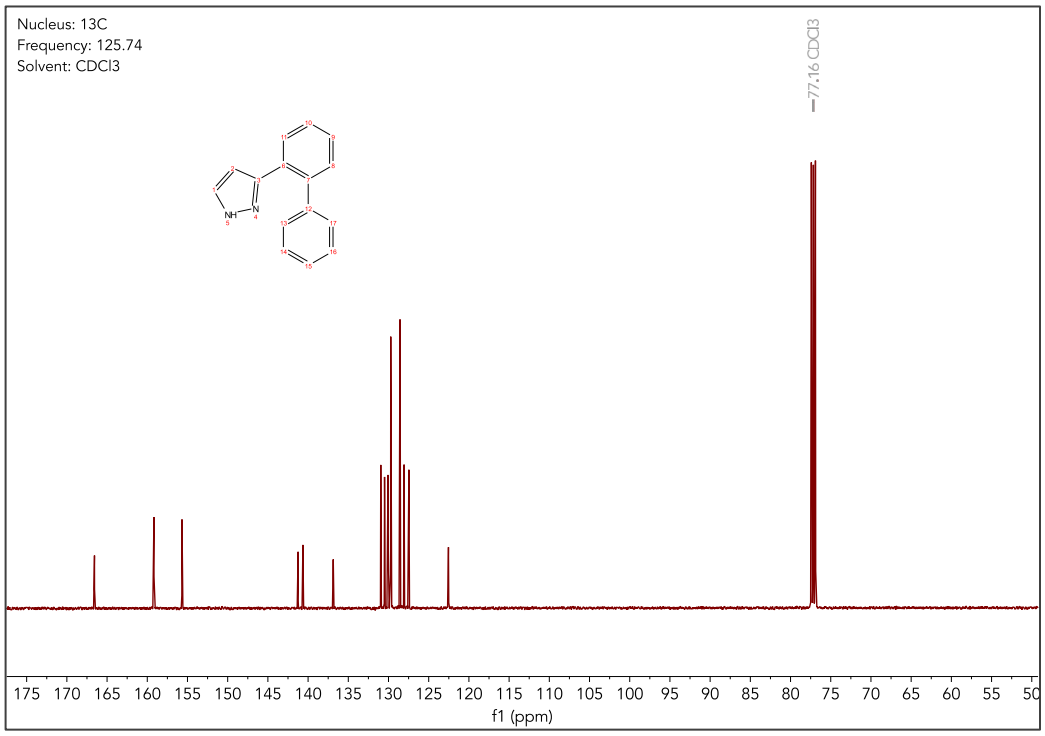

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
2.16
2.21
1.00
1.03
3.64
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

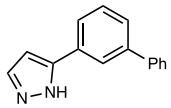
Compound **3a**

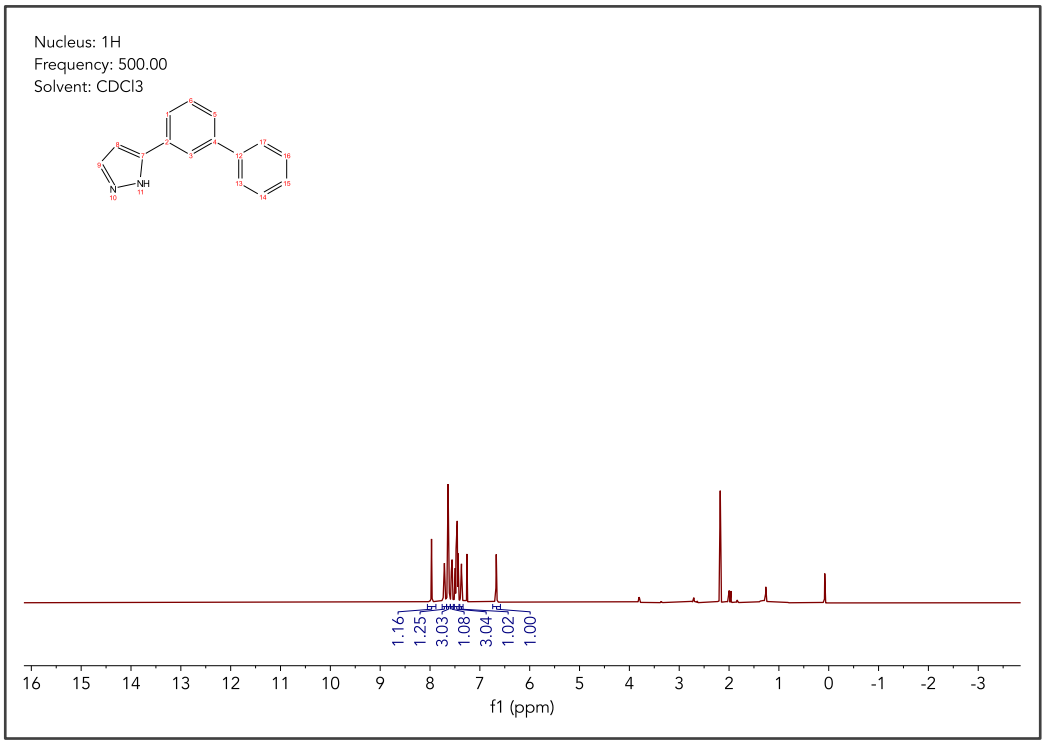

NH
N
Ph

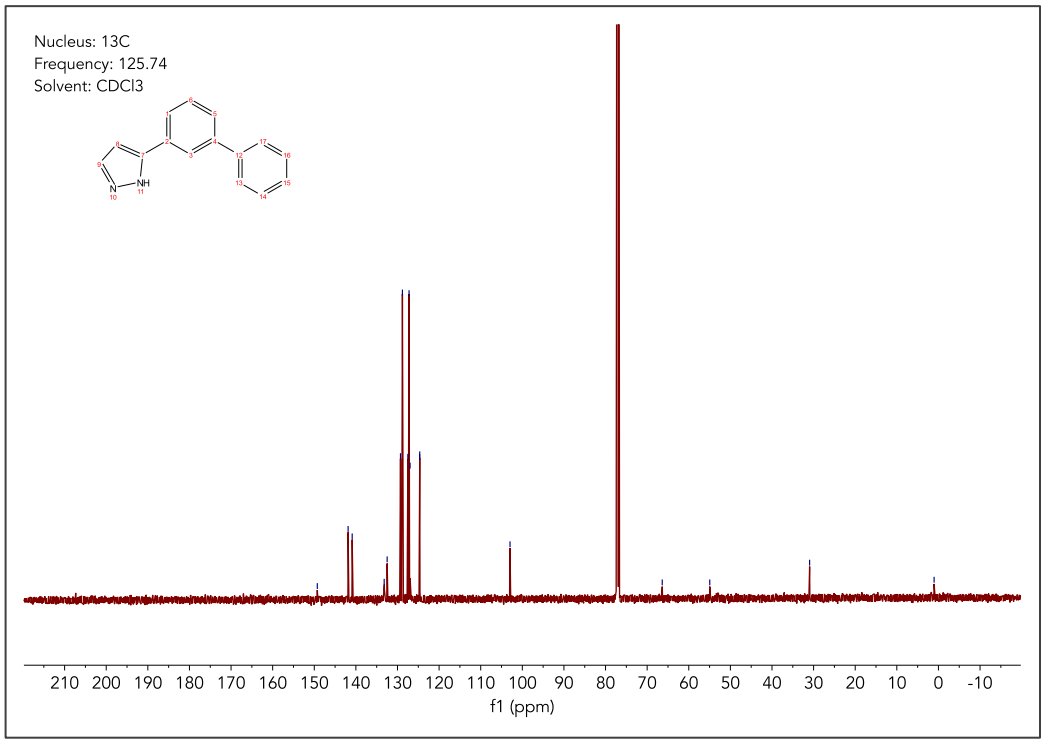

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
7.26 CDCl3
1.00
1.01
0.99
2.03
1.00
2.95
2.03
0.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
77.16 CDCl3
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50
f1 (ppm)

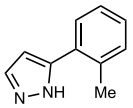
Compound **3b**

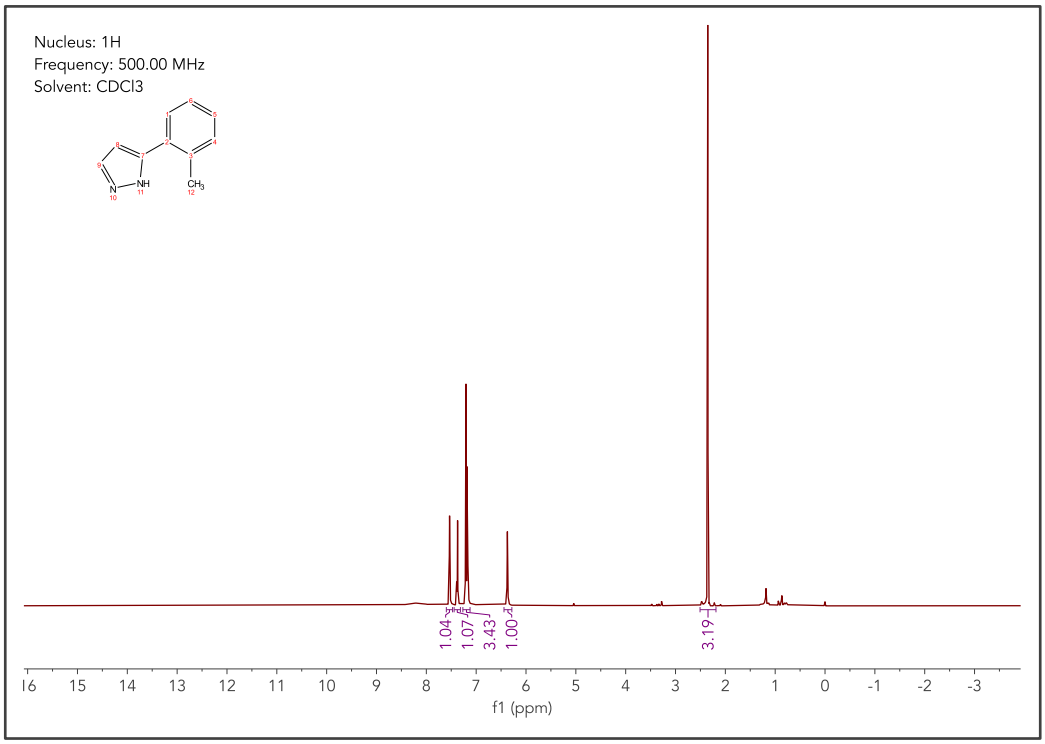

Ph
N
NH


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.16
1.25
3.03
1.08
3.04
1.02
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

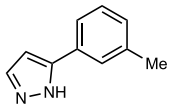

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

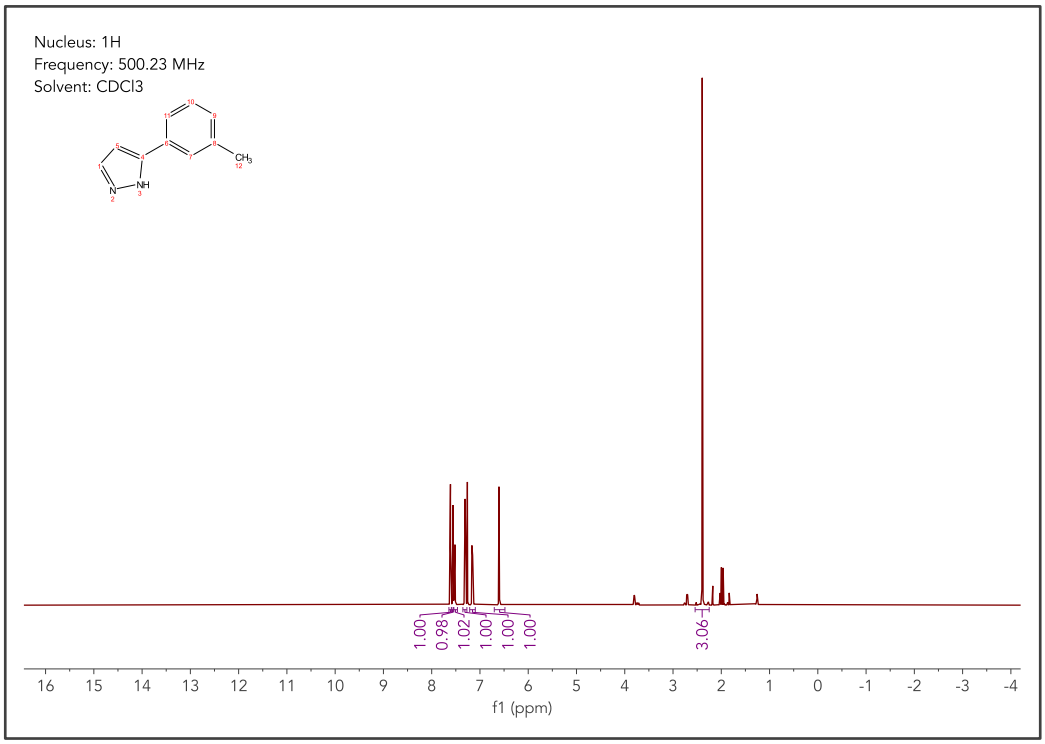
Compound **5a**

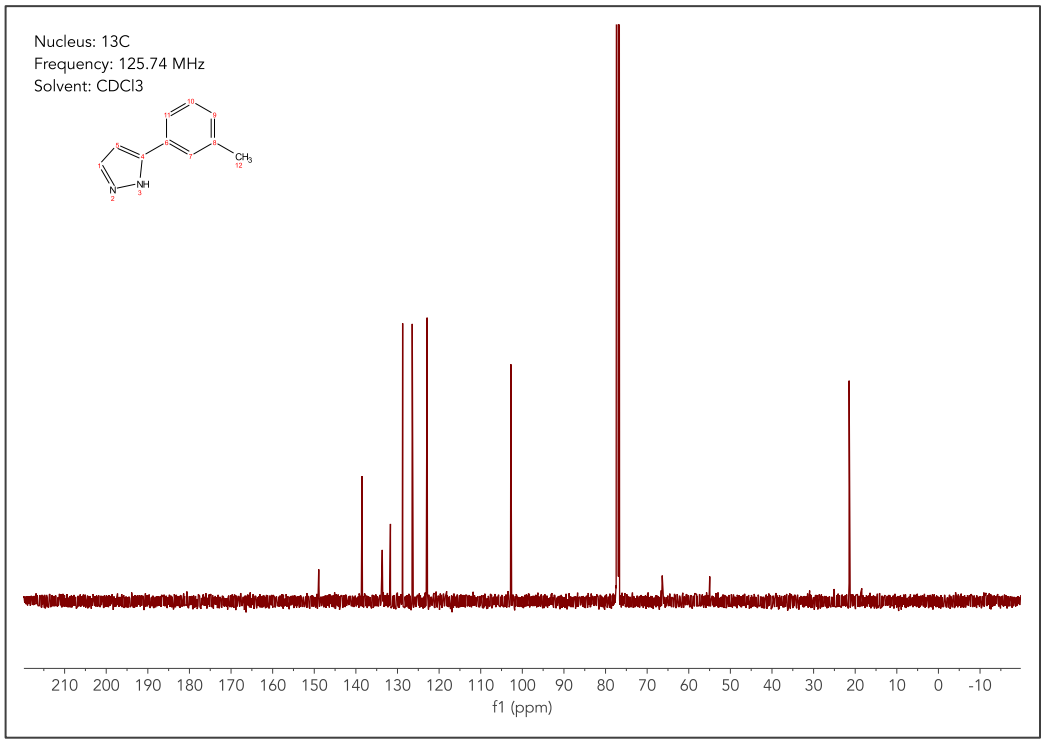

NH
N
Me


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.04
1.07
3.43
1.00
3.19
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

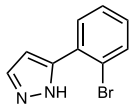
Compound **4b**

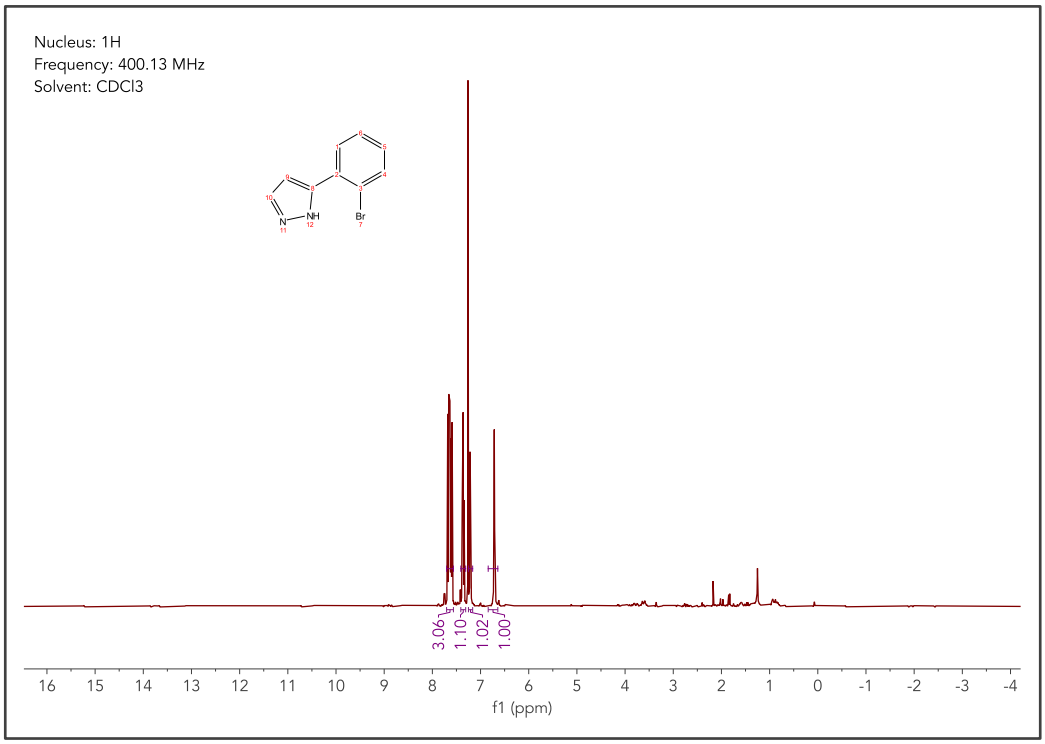

Me
N
NH


Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
1.00
0.98
1.02
1.00
1.00
1.00
3.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

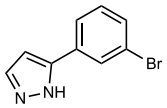

Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

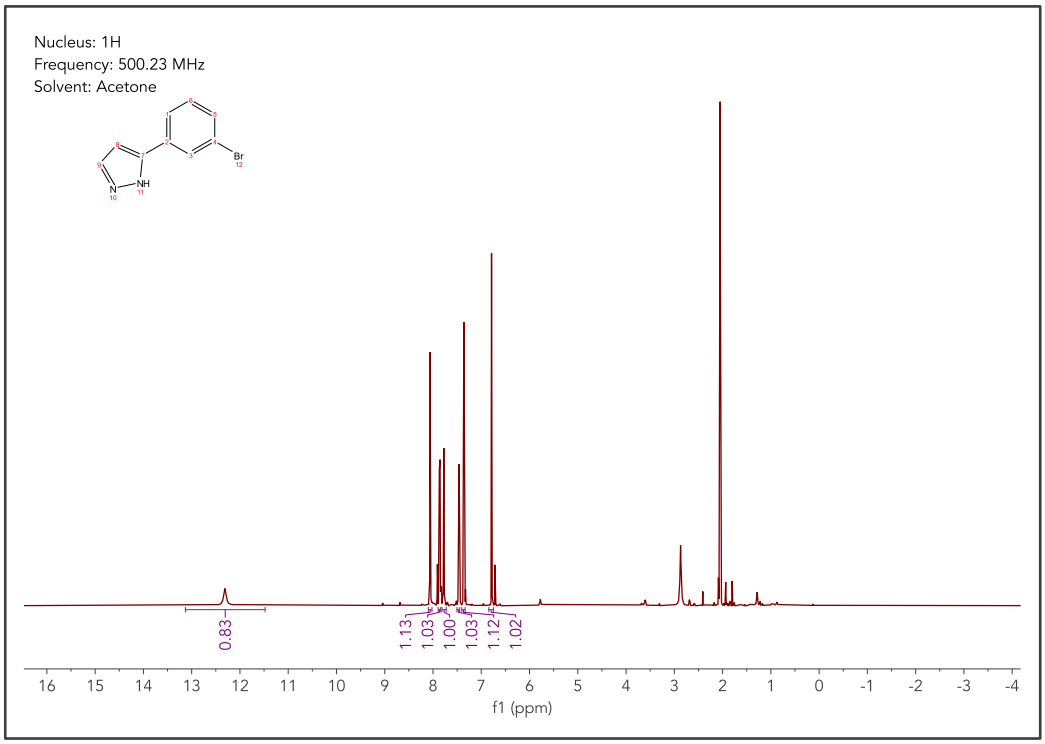
Compound **5a**


N
NH
Br

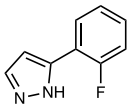

Nucleus: 1H
Frequency: 400.13 MHz
Solvent: CDCl3
3.06
1.10
1.02
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

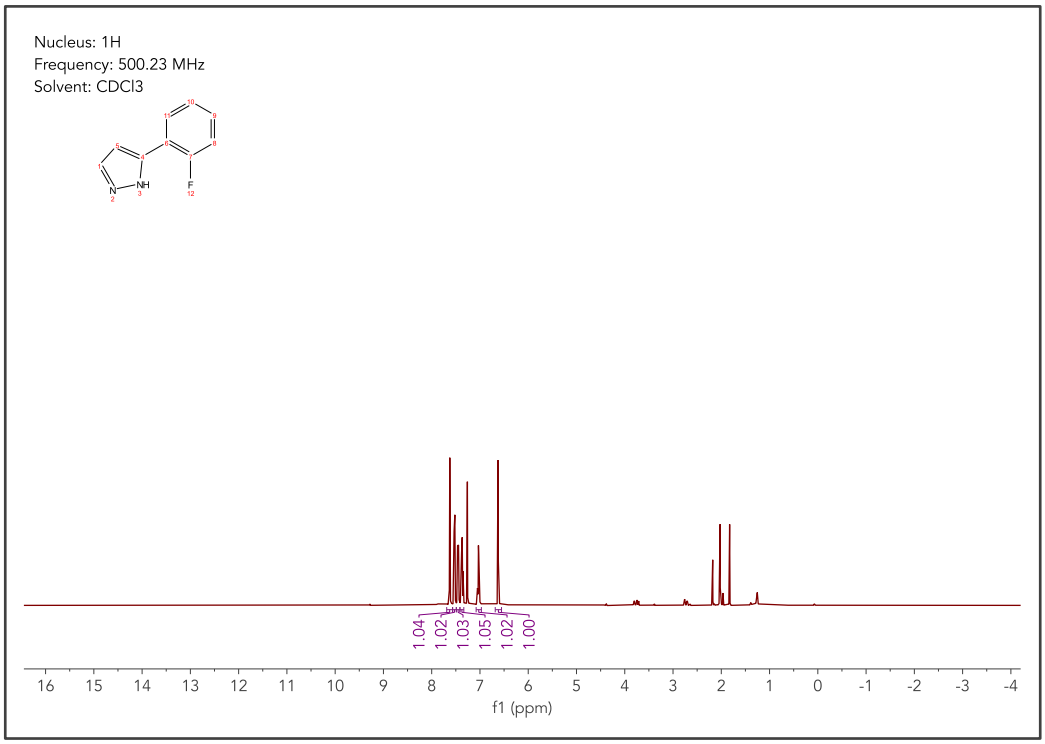
Compound **5b**

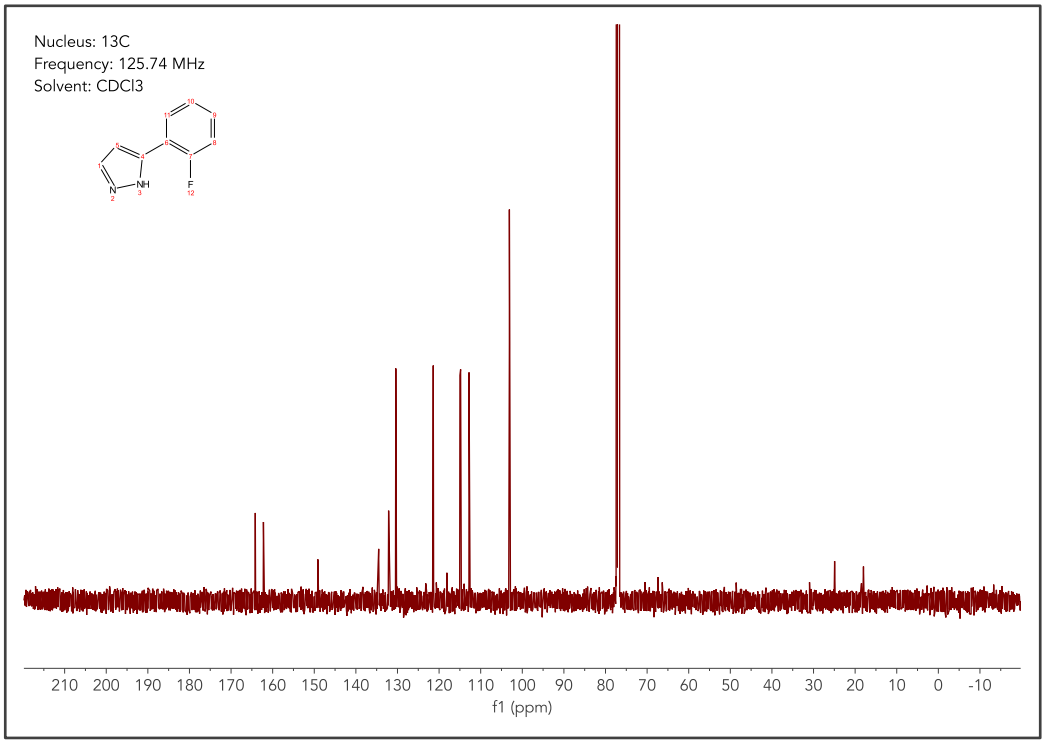

Br
N
NH


Nucleus: 1H
Frequency: 500.23 MHz
Solvent: Acetone
Br
NH
0.83
1.13
1.03
1.00
1.03
1.12
1.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

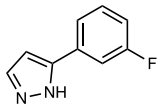
Compound **6a**

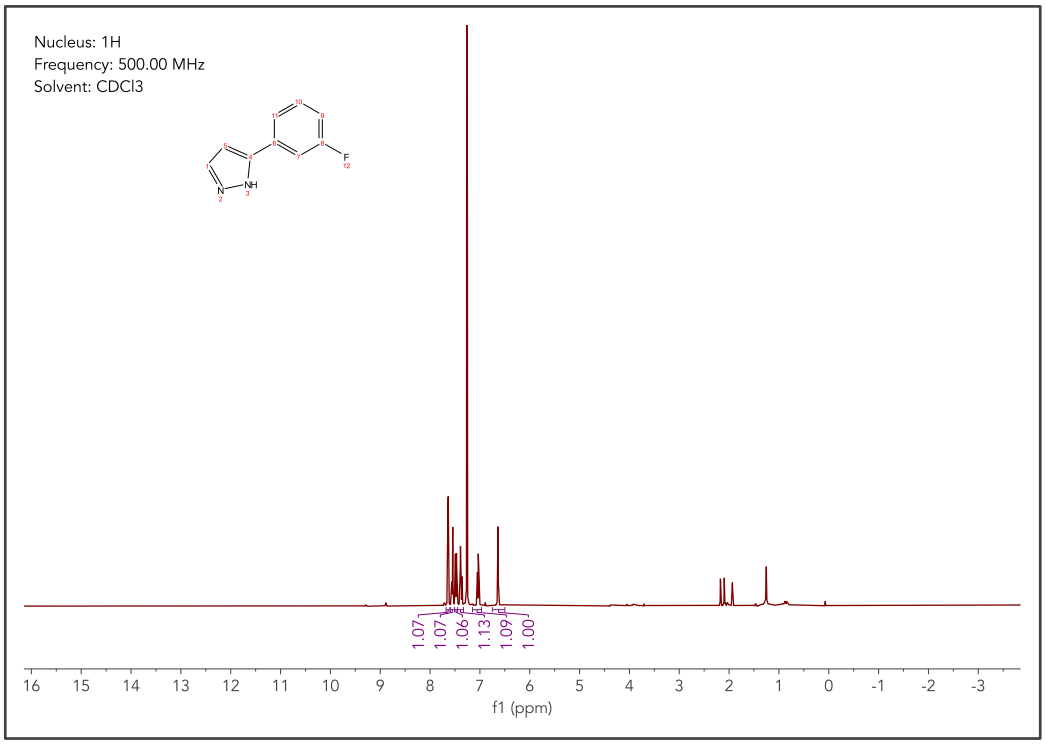

N
NH
F


Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
1.04
1.02
1.03
1.05
1.02
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

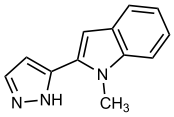

Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

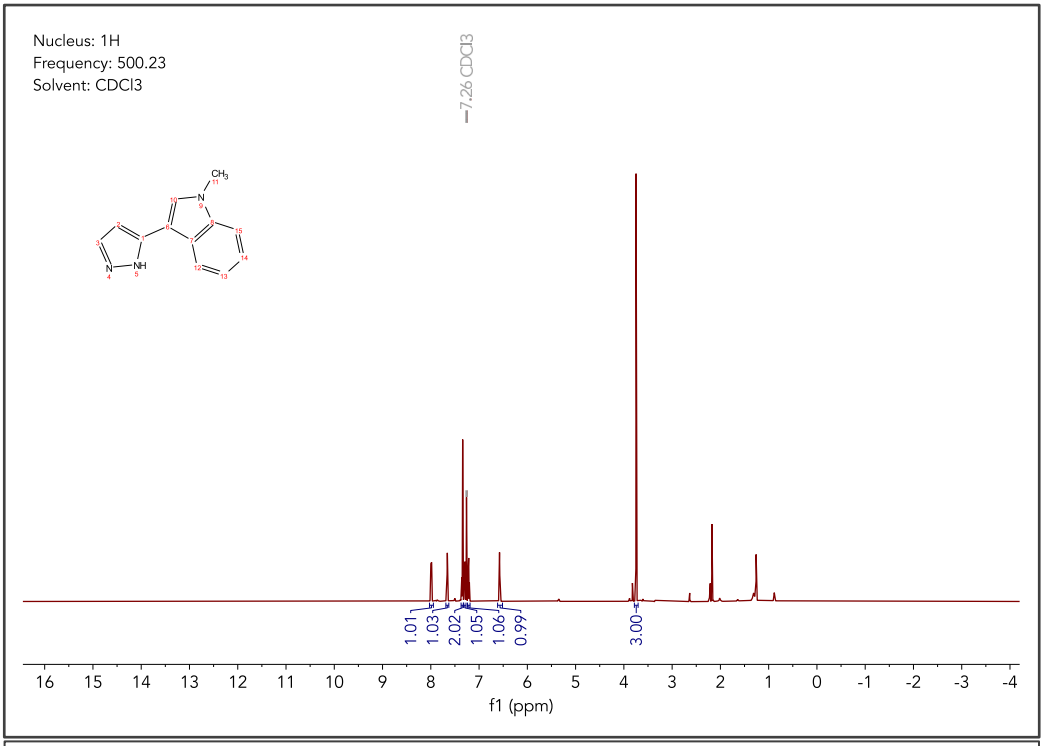
Compound **6b**

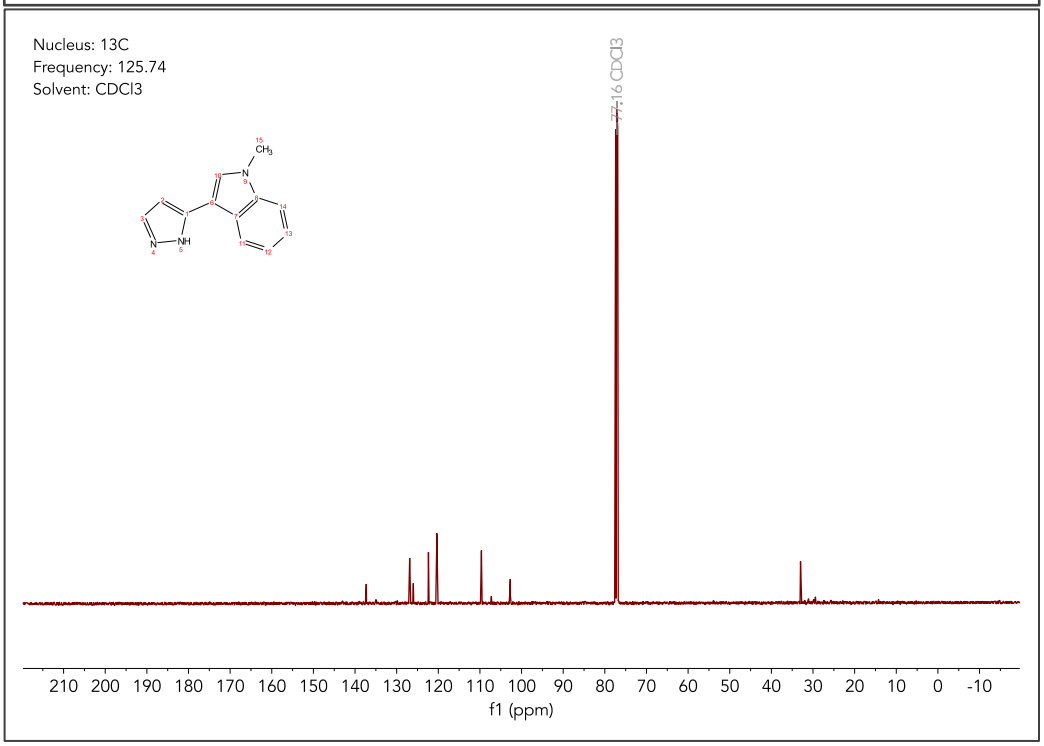

F
N
NH


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.07
1.07
1.06
1.13
1.09
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

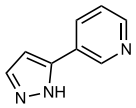
Compound **7**

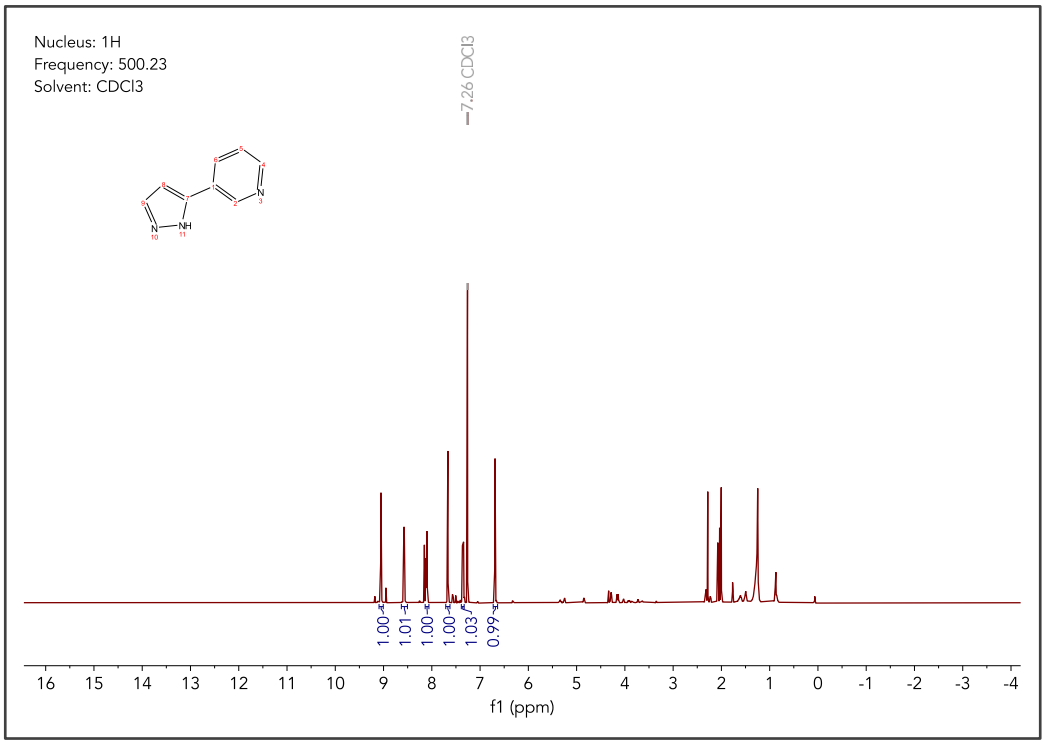

N
NH
CH3


Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
7.26 CDCl3
1.01
1.03
2.02
1.05
1.06
0.99
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

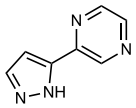

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
77.16 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

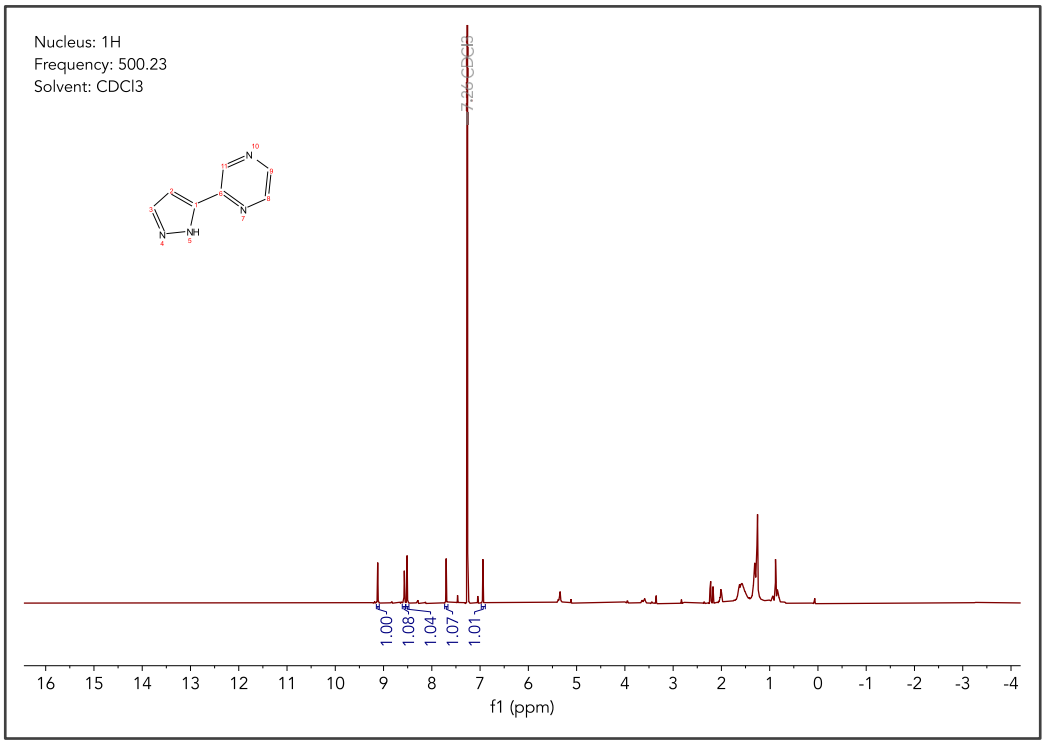
Compound **8a**


N
N
NH

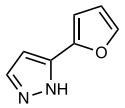

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
7.26 CDCl3
1.00
1.01
1.00
1.00
1.03
0.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

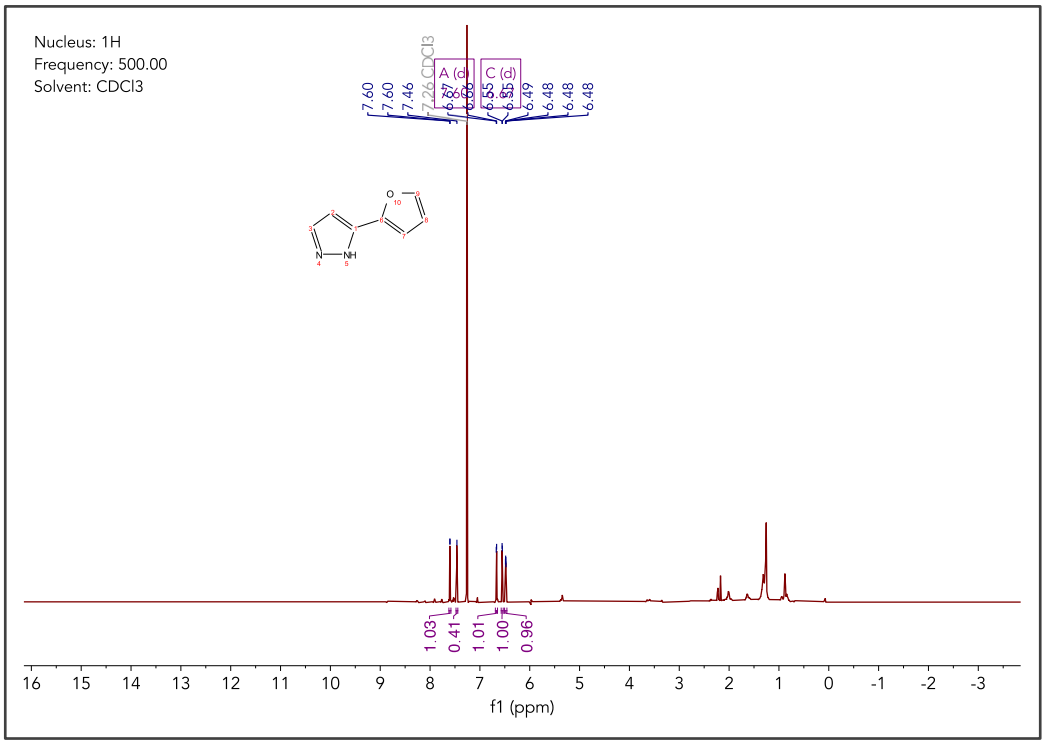
Compound **8b**



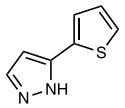

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
7.26 CDCl3
1.00
1.08
1.04
1.07
1.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

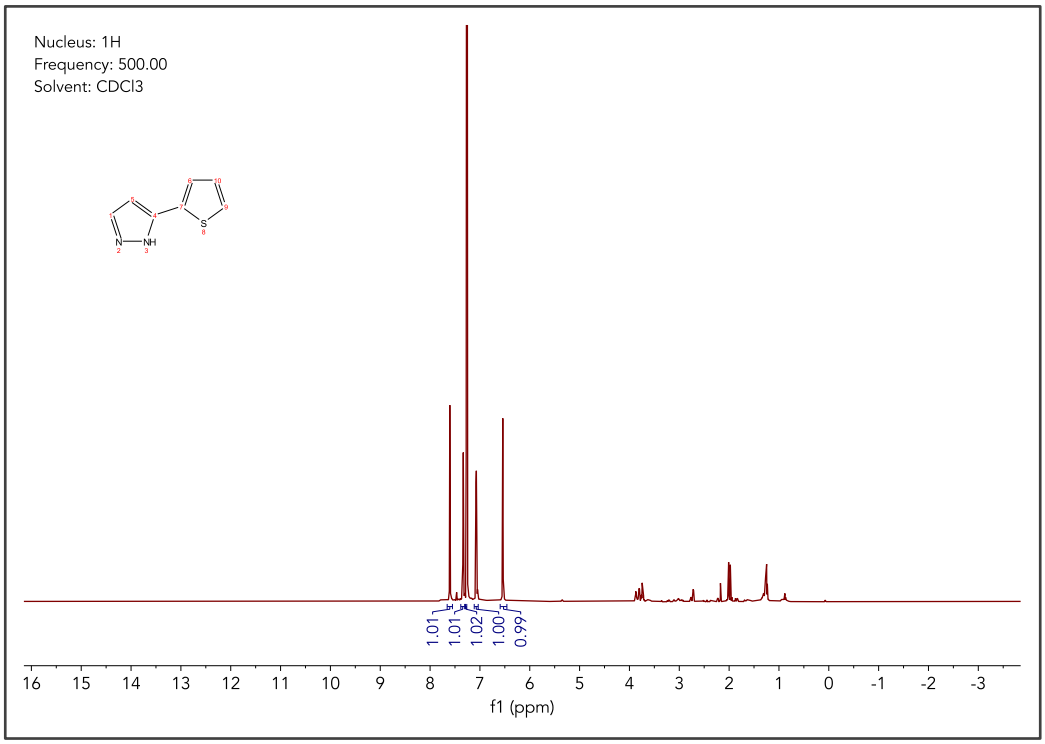
Compound **9**

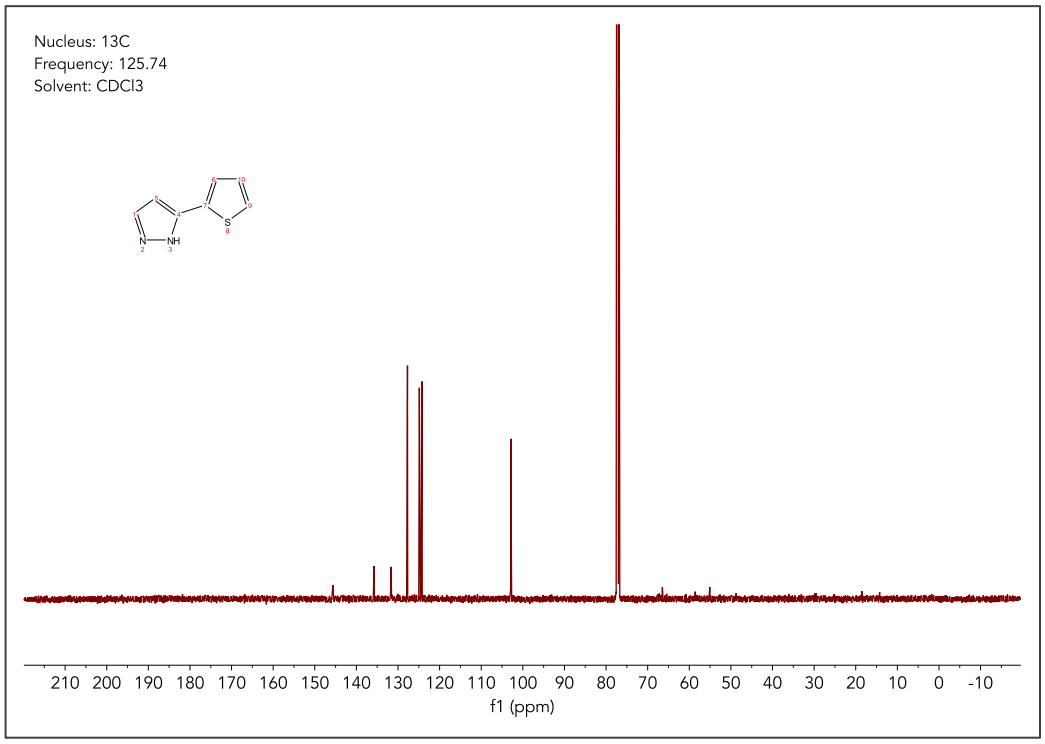

O
N
NH


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
7.60
7.60
7.46
7.26 CDCl3
6.87
6.87
6.55
6.55
6.49
6.48
6.48
6.48
A (d)
C (d)
1.03
0.41
1.01
1.00
0.96
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

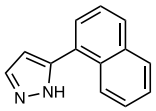
Compound **10**

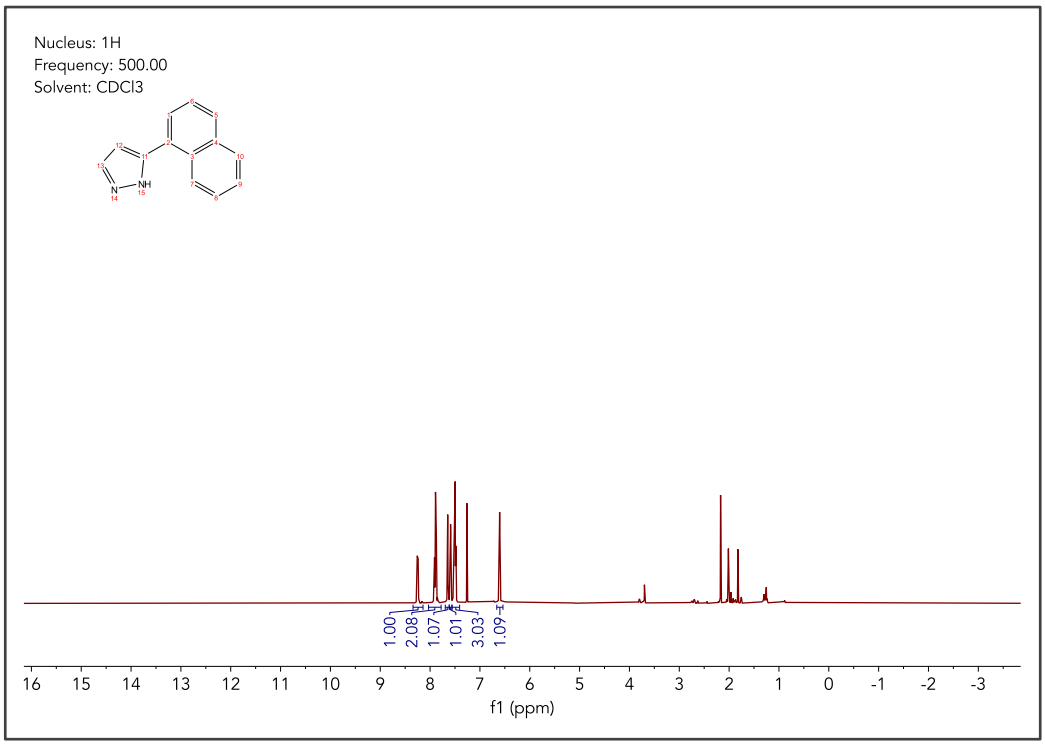

S
N
NH

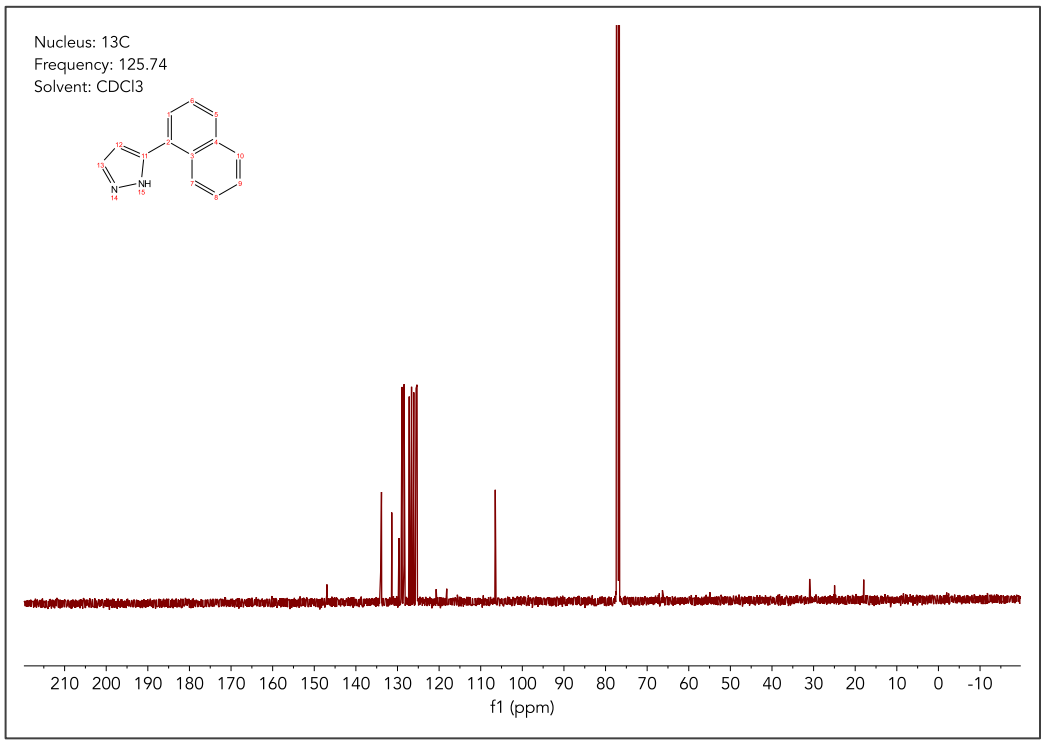

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.01
1.01
1.02
1.00
0.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

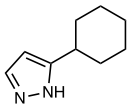
Compound **11**

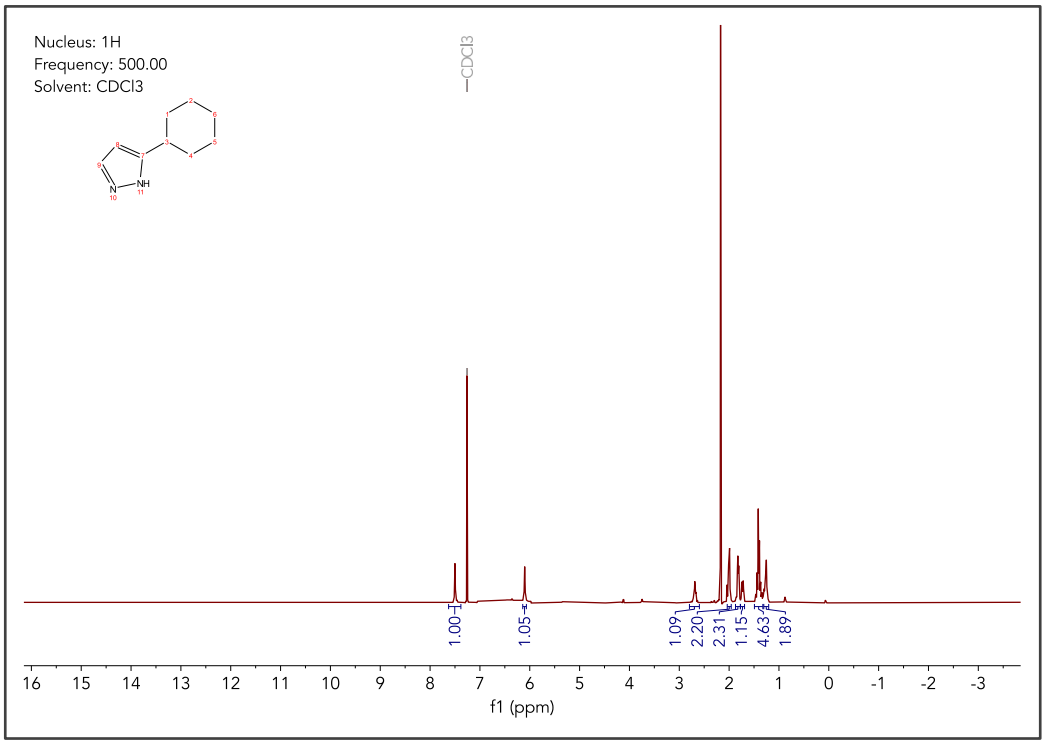

N
NH


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.00
2.08
1.07
1.01
3.03
1.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

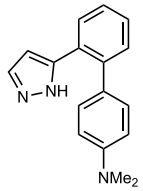

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

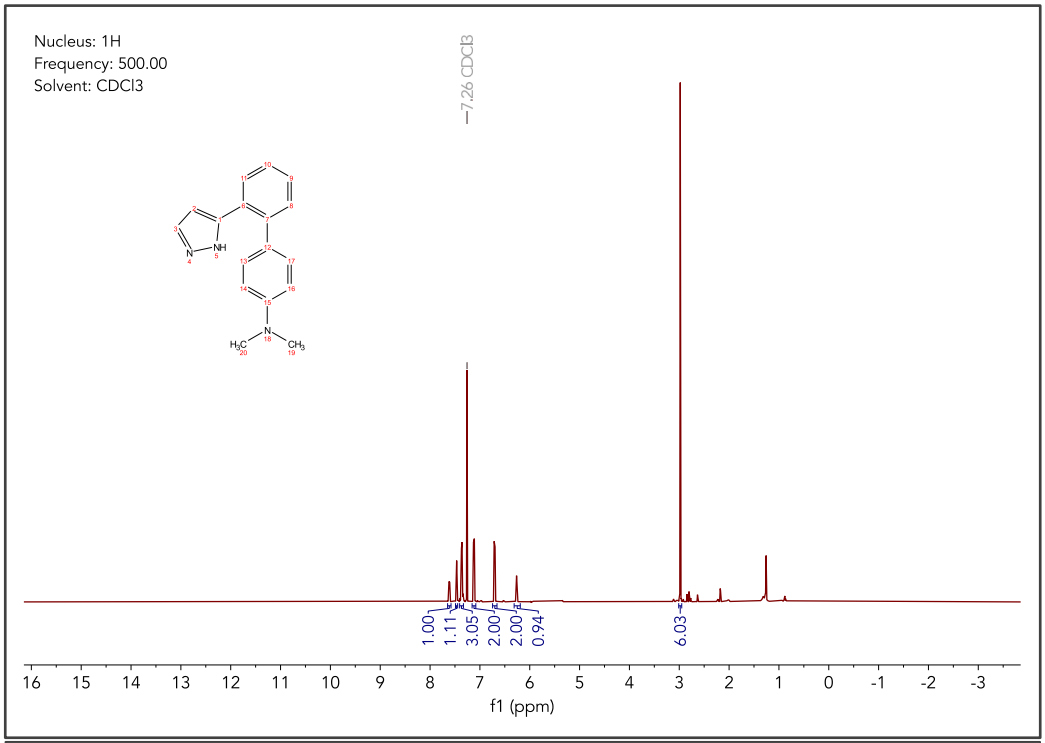
Compound **12**

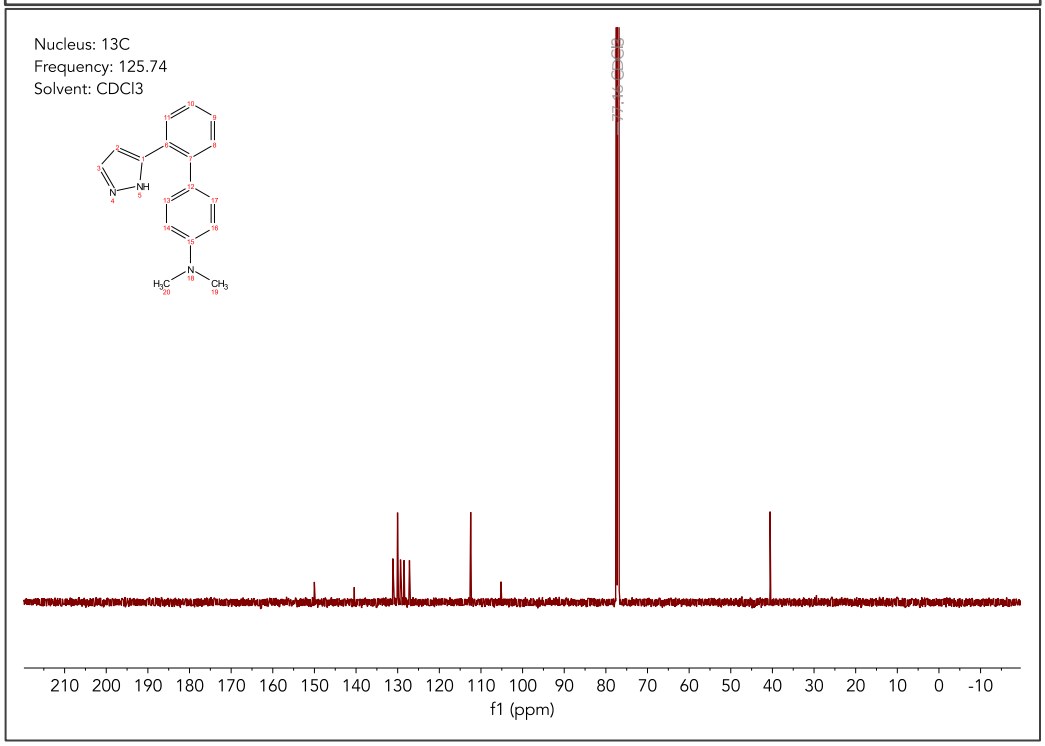

N
NH


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
CDCl3
1.00
1.05
1.09
2.20
2.31
1.15
4.63
1.89
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

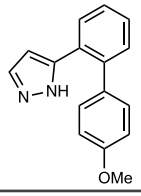
Compound **13**

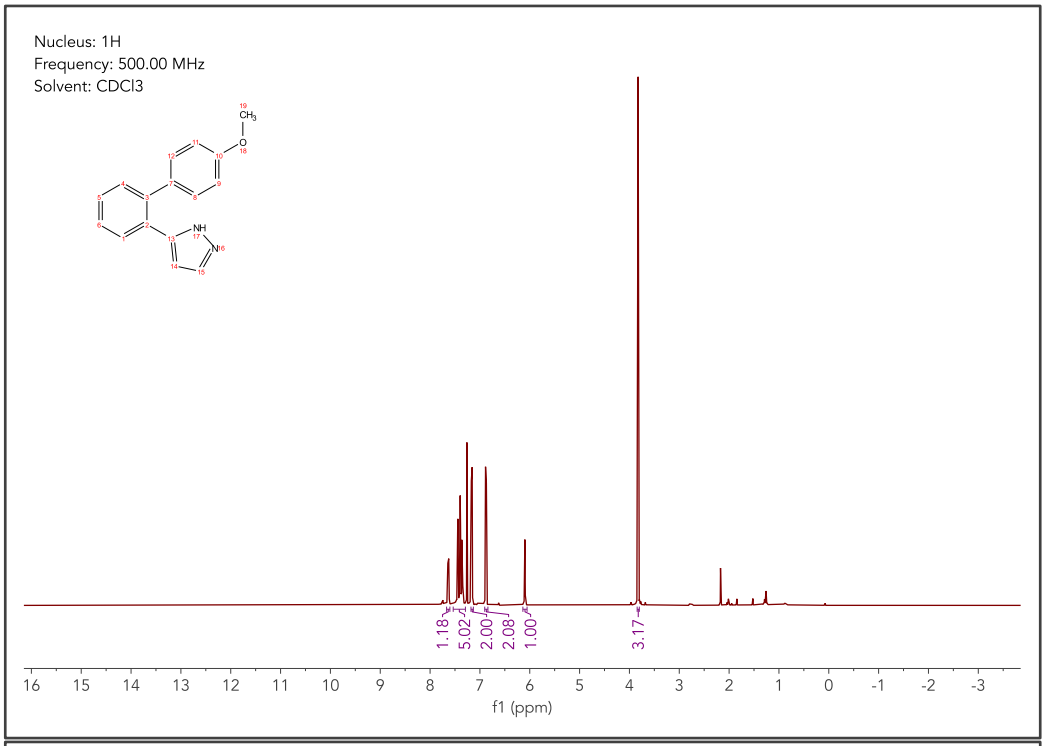

NH
NMe2

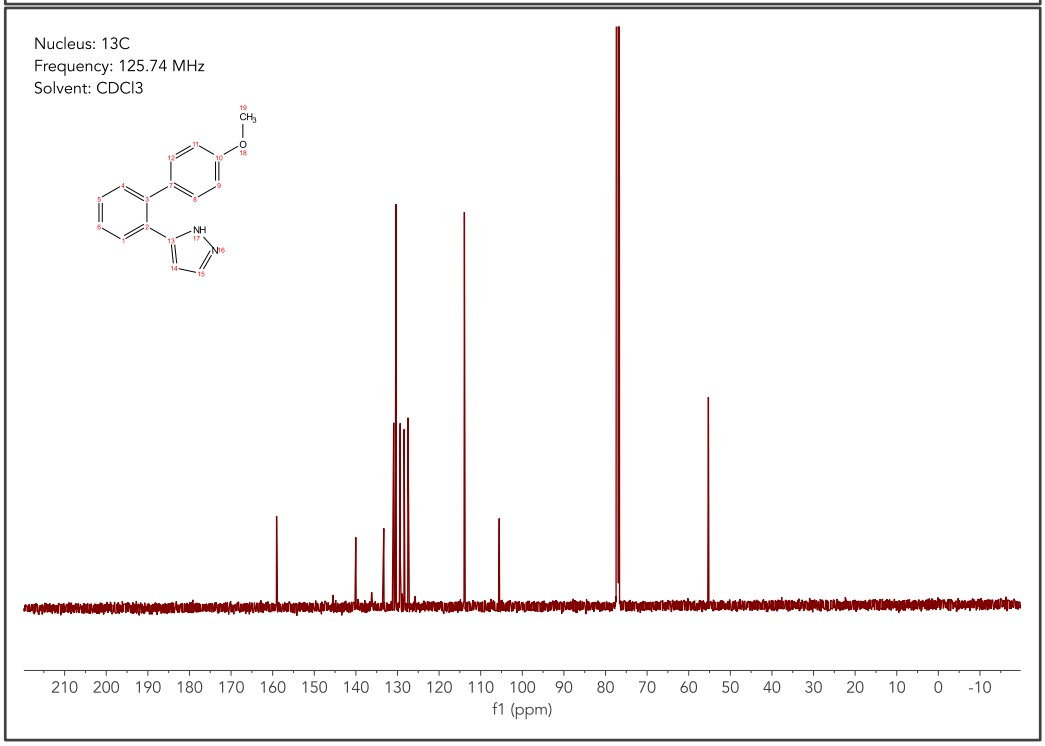

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
7.26 CDCl3
1.00
1.11
3.05
2.00
2.00
0.94
6.03
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
f1 (ppm)

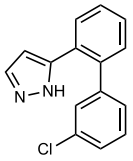
Compound **14**

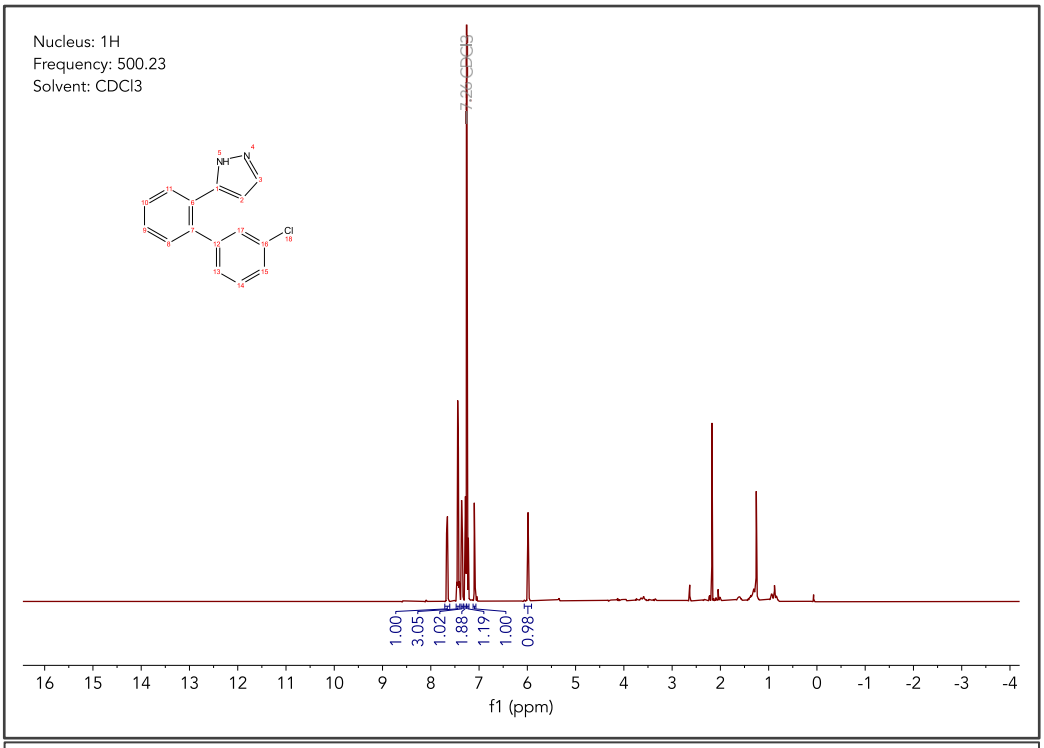

N
NH
OMe

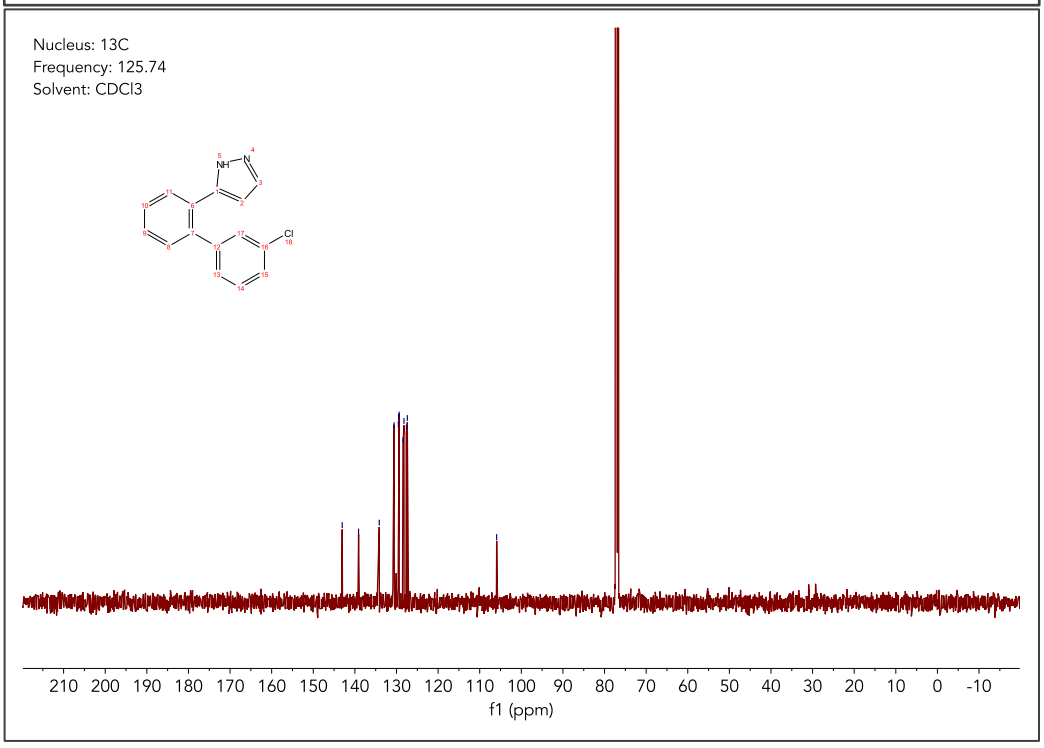

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.18
5.02
2.00
2.08
1.00
3.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

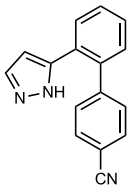
Compound **16**

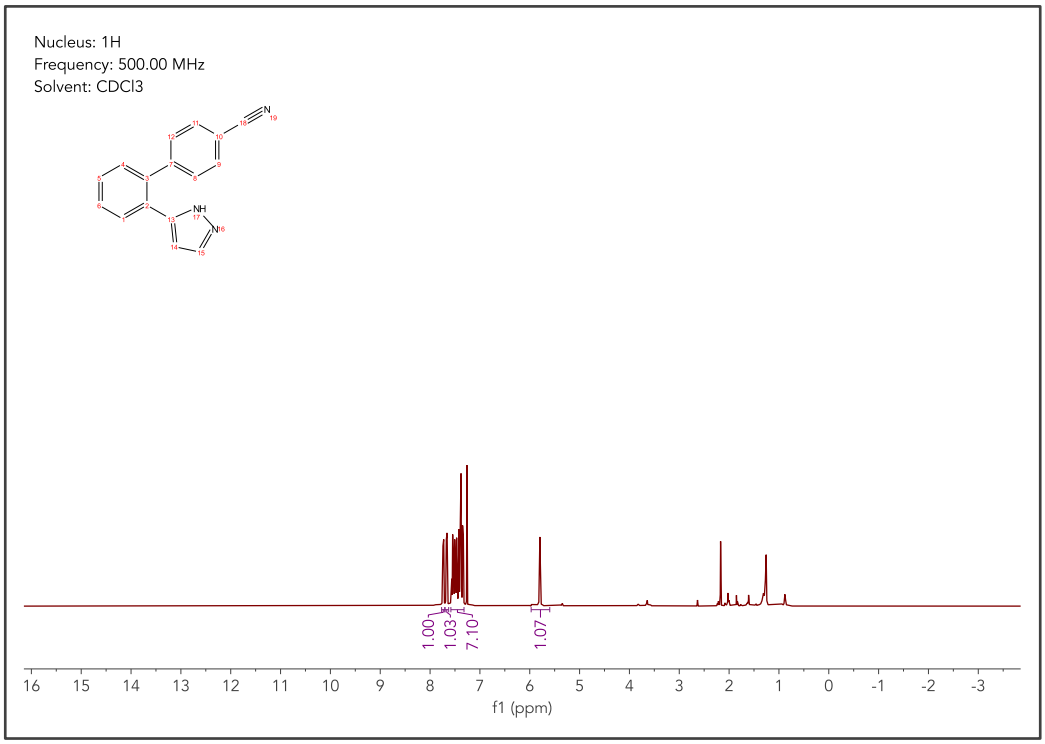

N
NH
Cl


Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
7.26 CDCl3
1.00
3.05
1.02
1.88
1.19
1.00
0.98
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

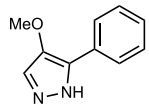

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

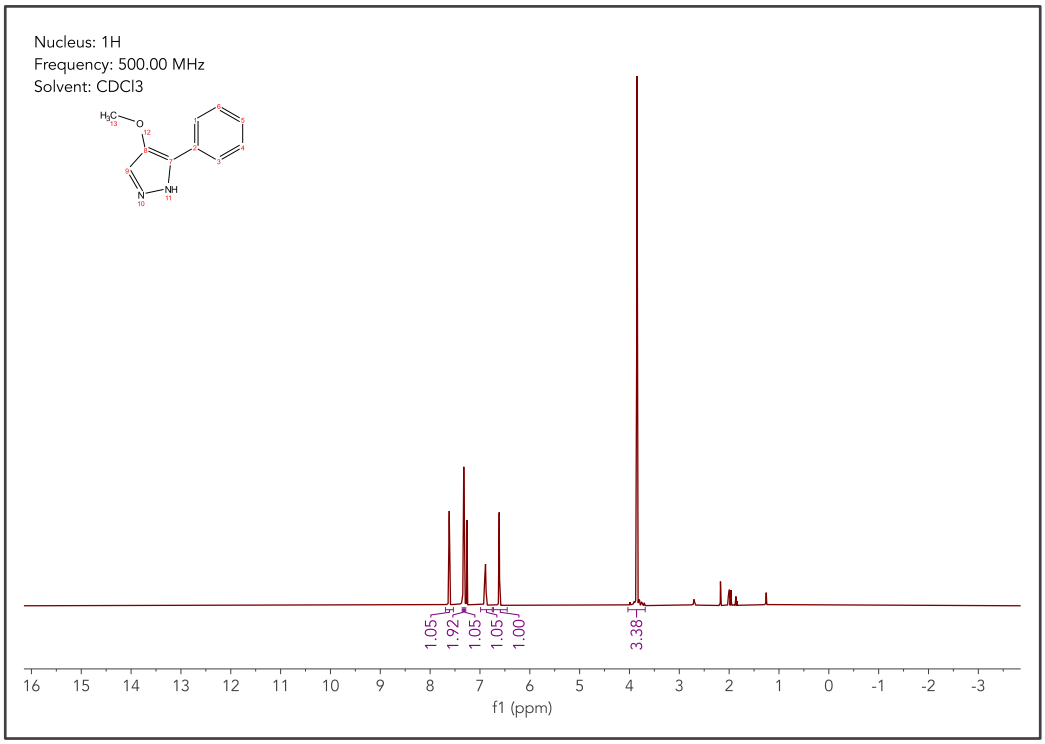
Compound **17**

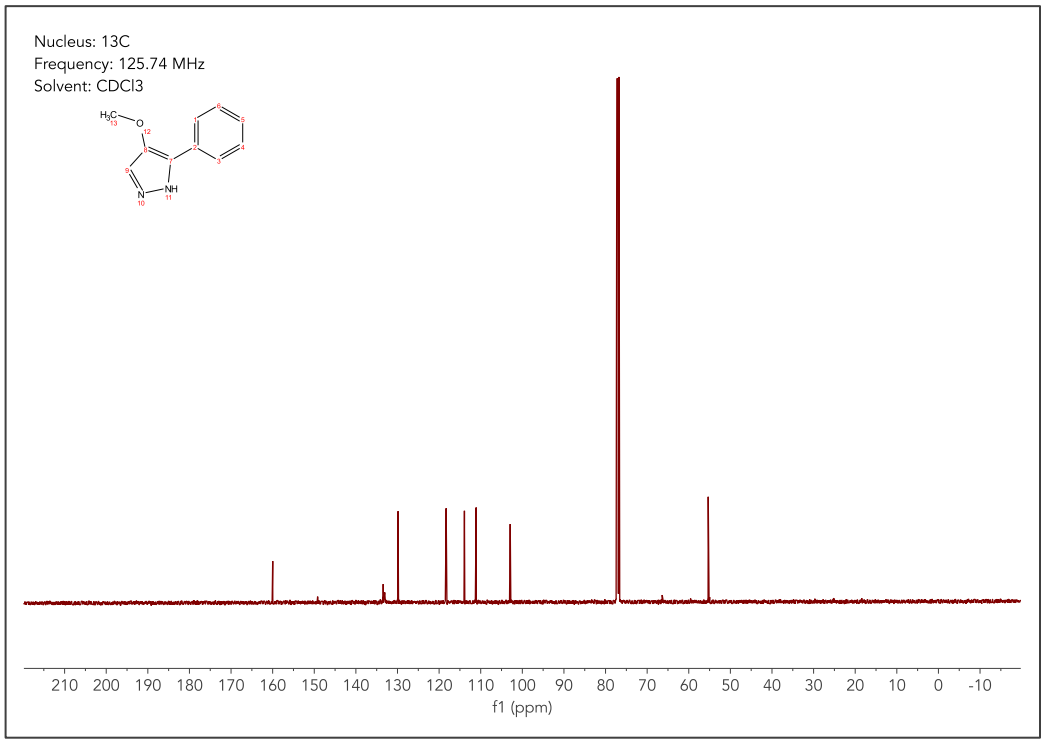

N
NH
CN


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.00
1.03
7.10
1.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

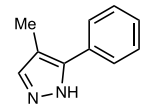
Compound **19**

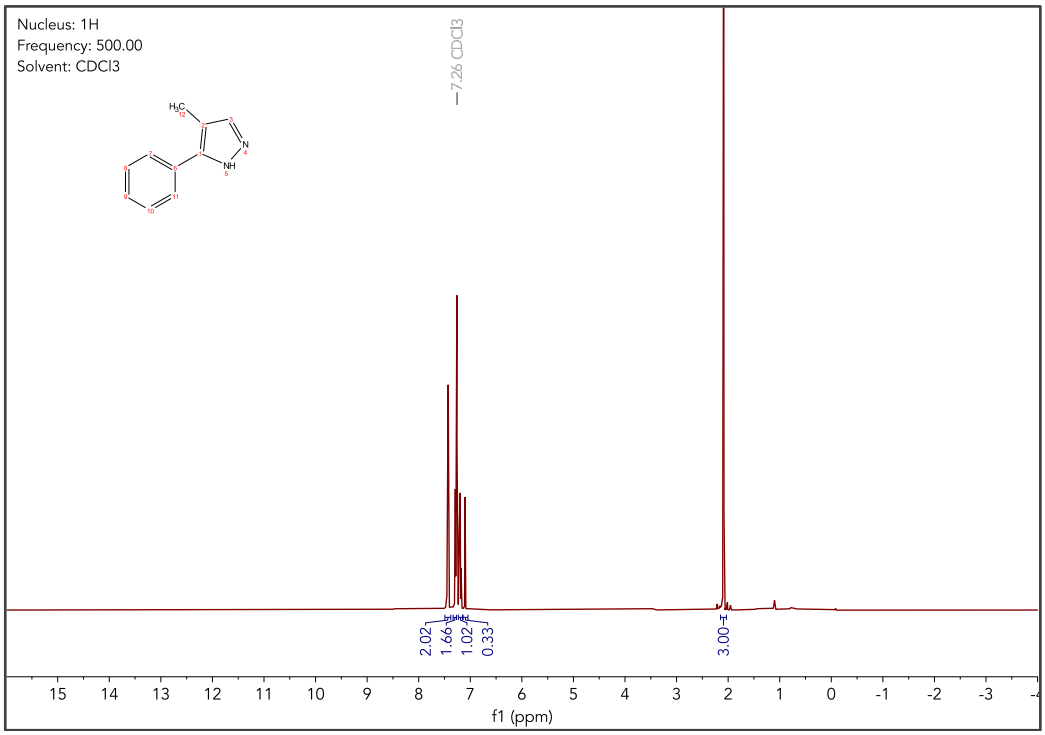

MeO
NH
N


Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.05
1.92
1.05
1.05
1.00
3.38
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

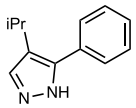

Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

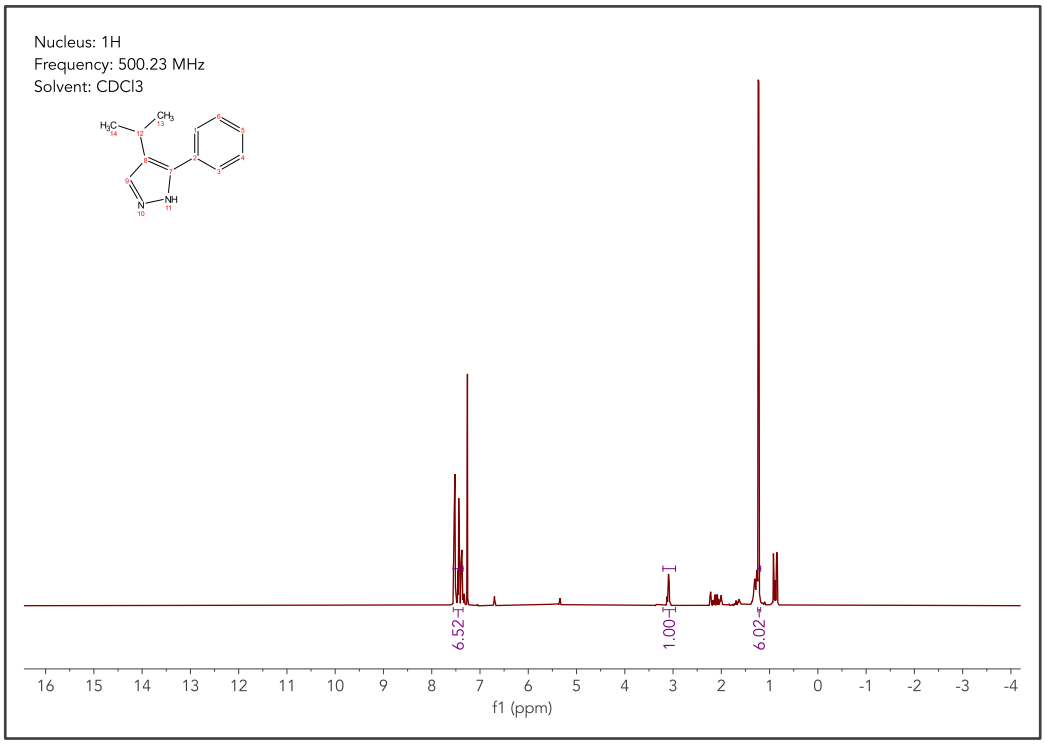
Compound **20**


Me
NH
N

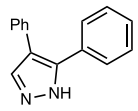

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
7.26 CDCl3
2.02
1.66
1.02
0.33
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

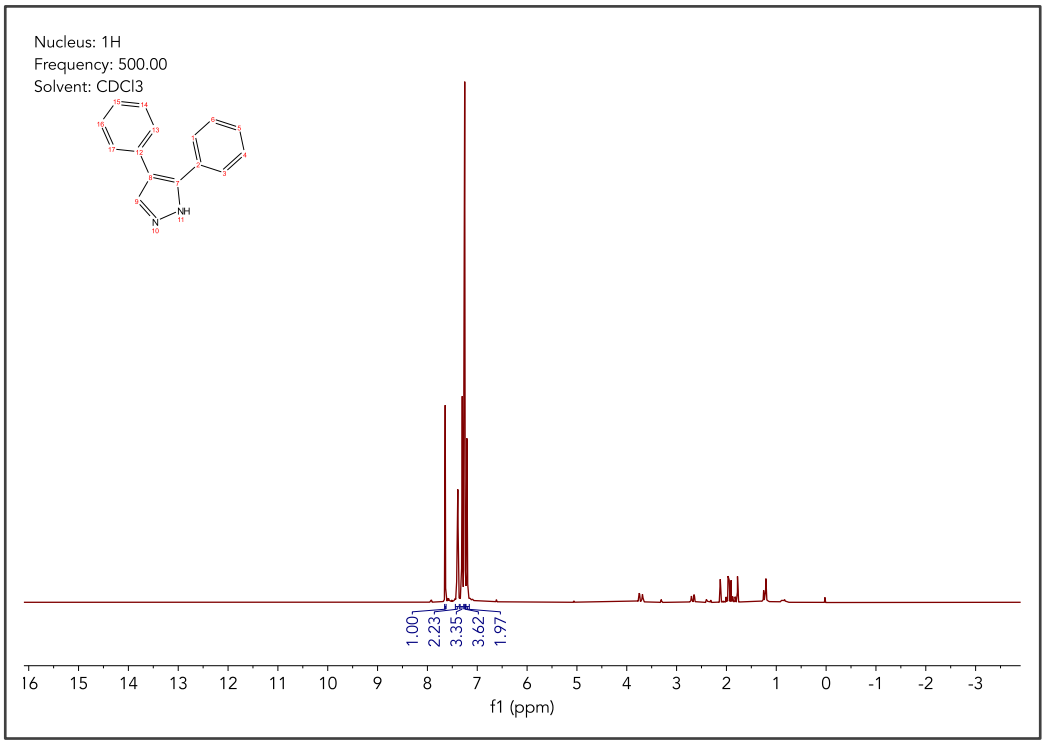
Compound **21**


iPr
N
NH

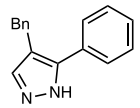

Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
6.52
1.00
6.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

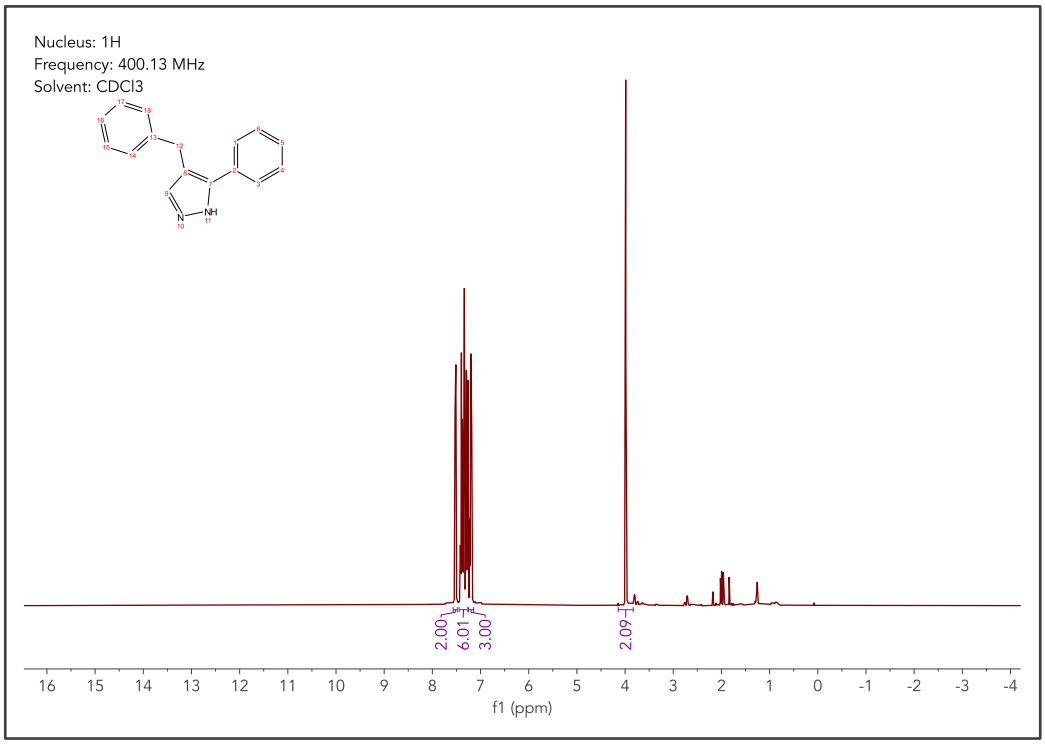
Compound **22**


Ph
NH
N

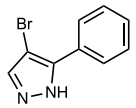

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.00
2.23
3.35
3.62
1.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

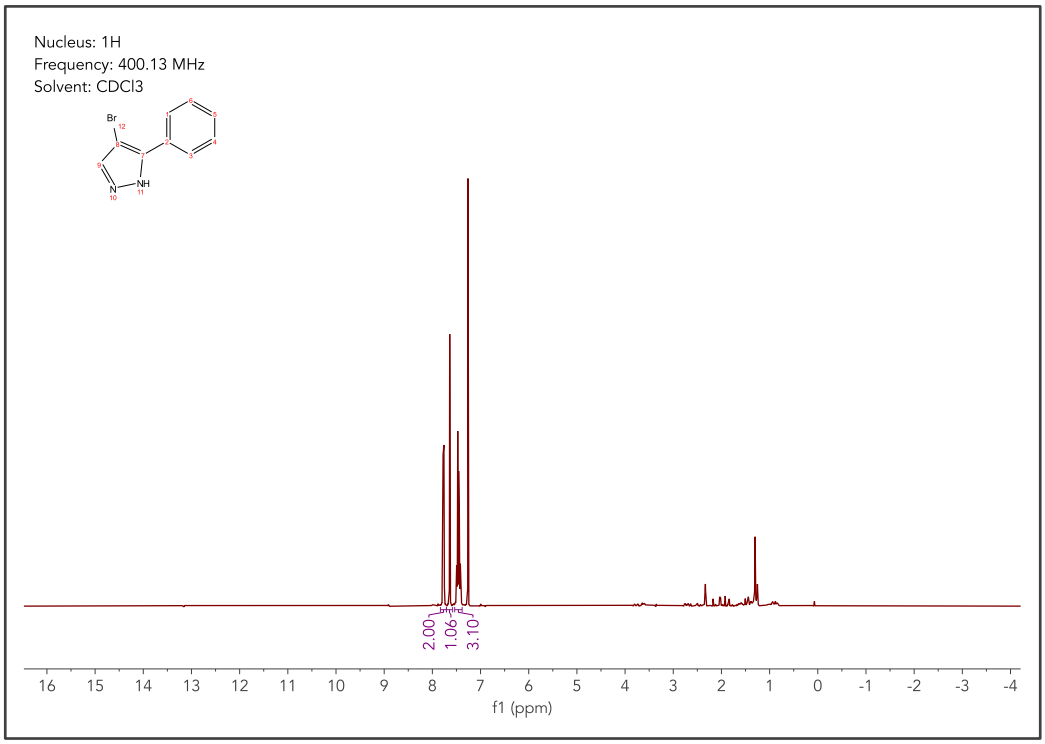
Compound **23**


Bn
NH
N

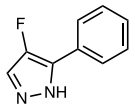

Nucleus: 1H
Frequency: 400.13 MHz
Solvent: CDCl3
2.00
6.01
3.00
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

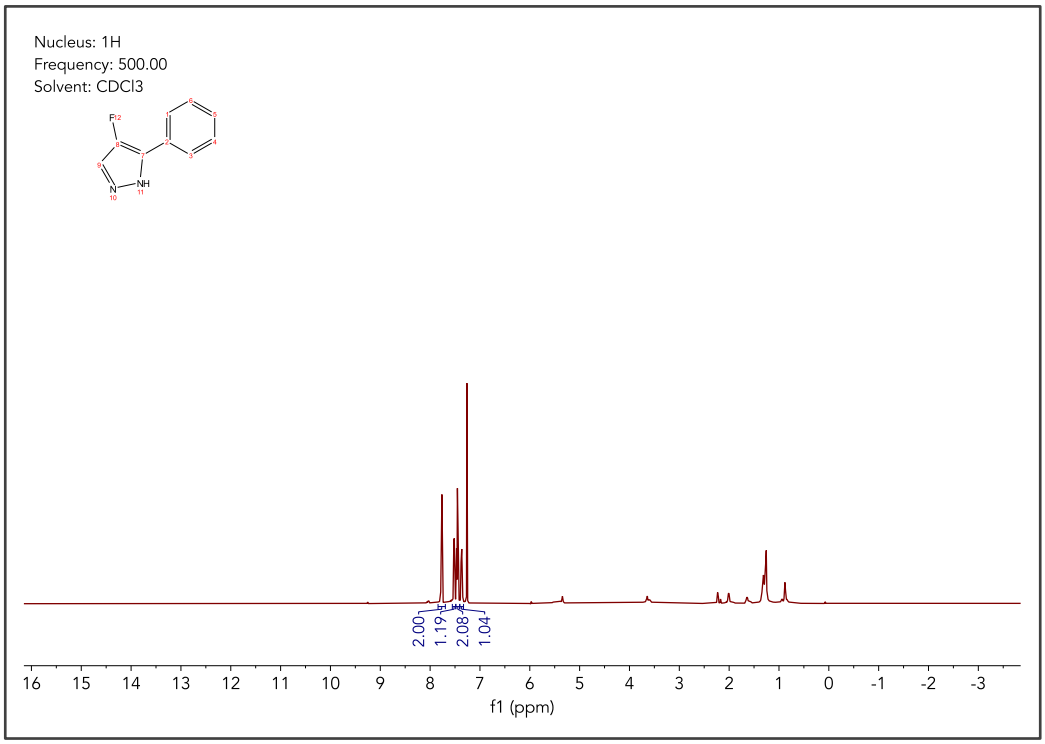
Compound **24**


Br
NH
N

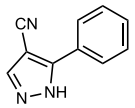

Nucleus: 1H
Frequency: 400.13 MHz
Solvent: CDCl3
2.00
1.06
3.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

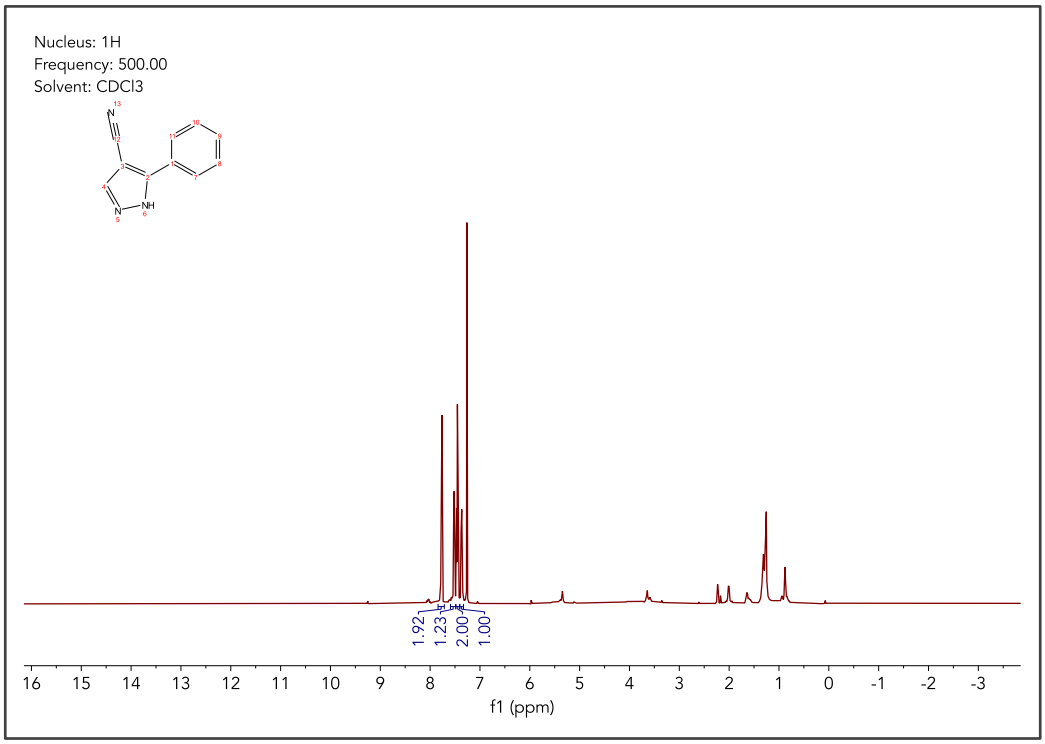
Compound **25**


F
NH
N

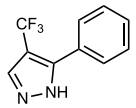

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
2.00
1.19
2.08
1.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

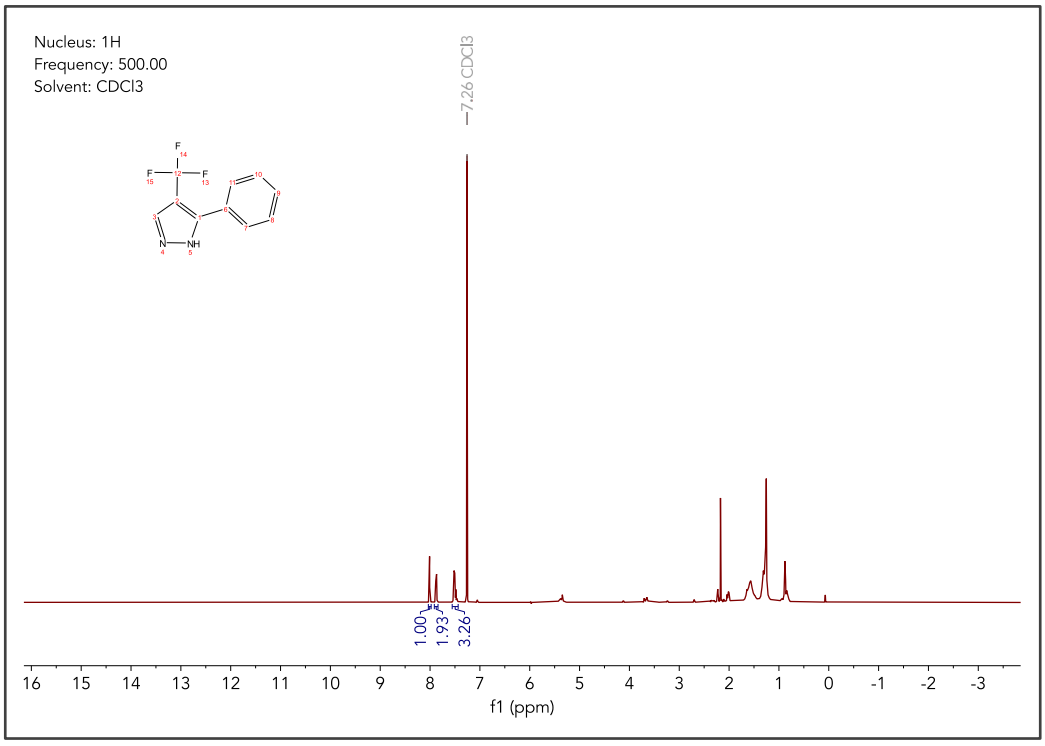
Compound **26**


CN
NH
N

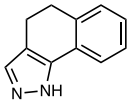

Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.92
1.23
2.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

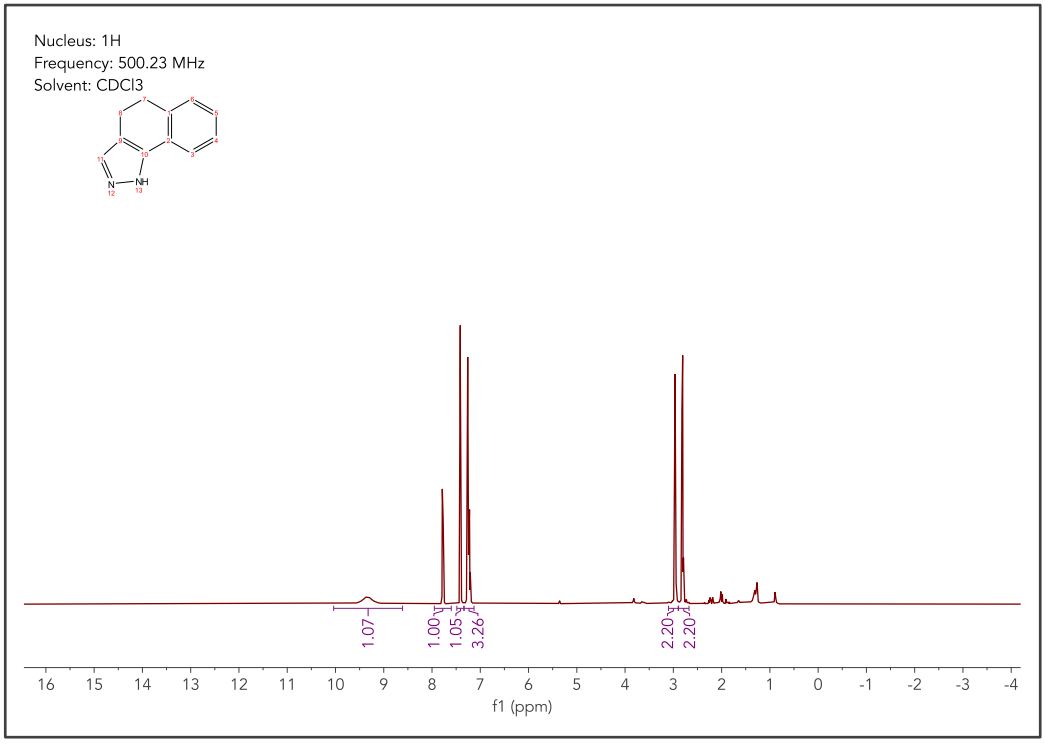
Compound **27**

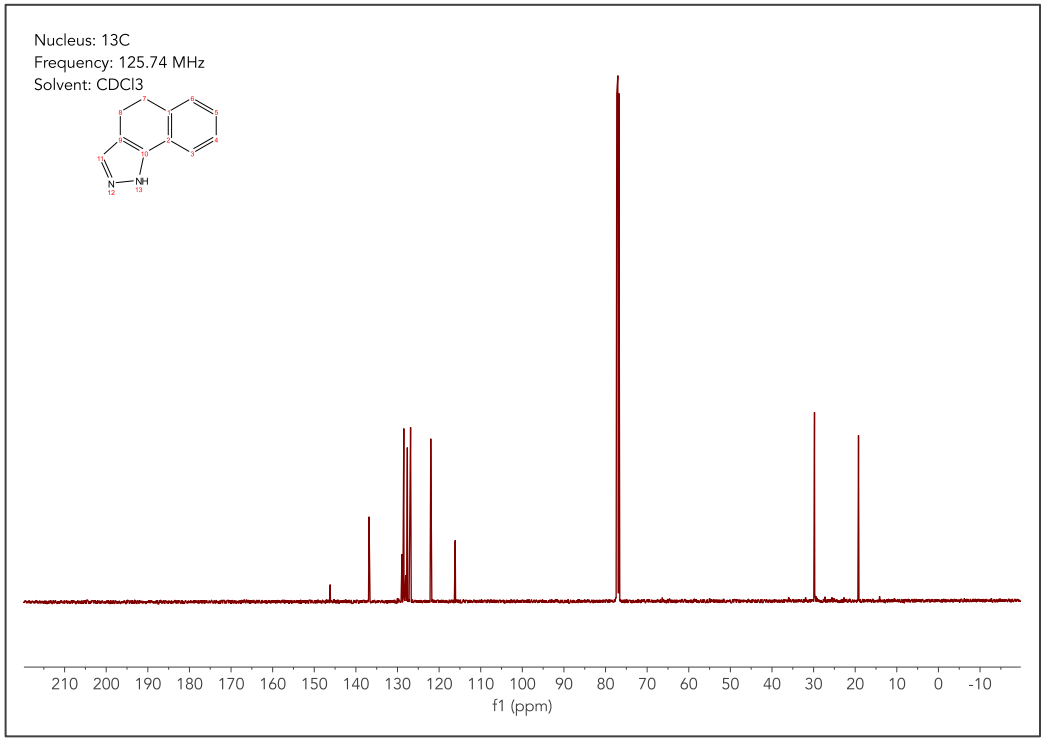

CF3
NH
N


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
7.26 CDCl3
1.00
1.93
3.26
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

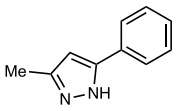
Compound **28**

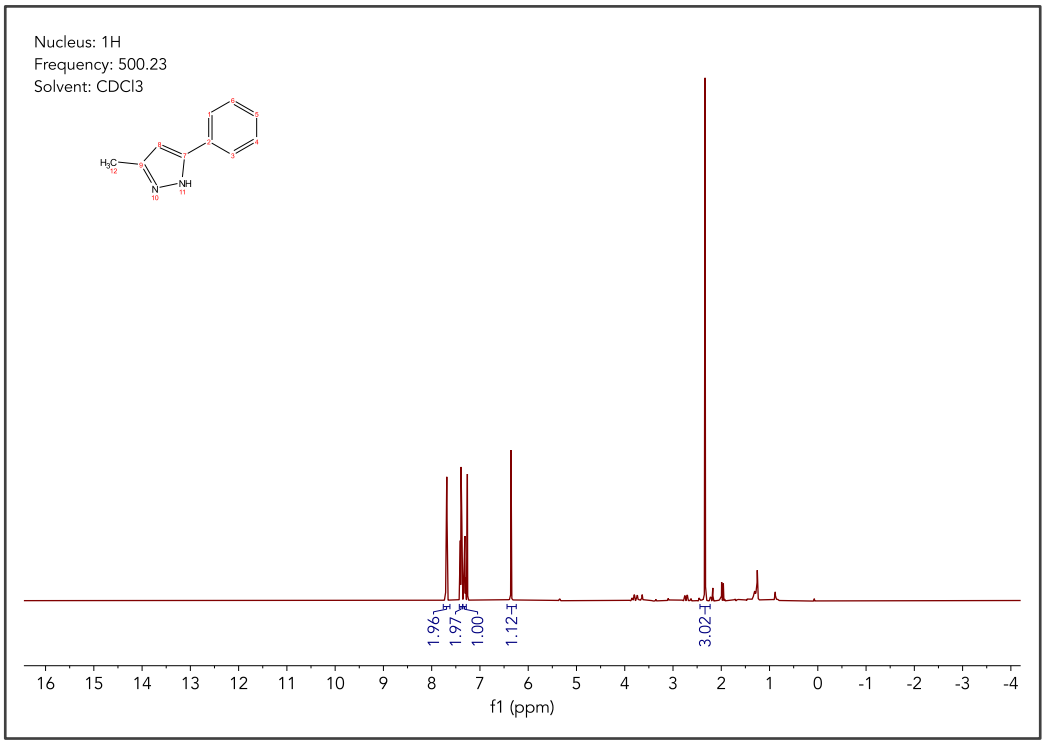

N—NH

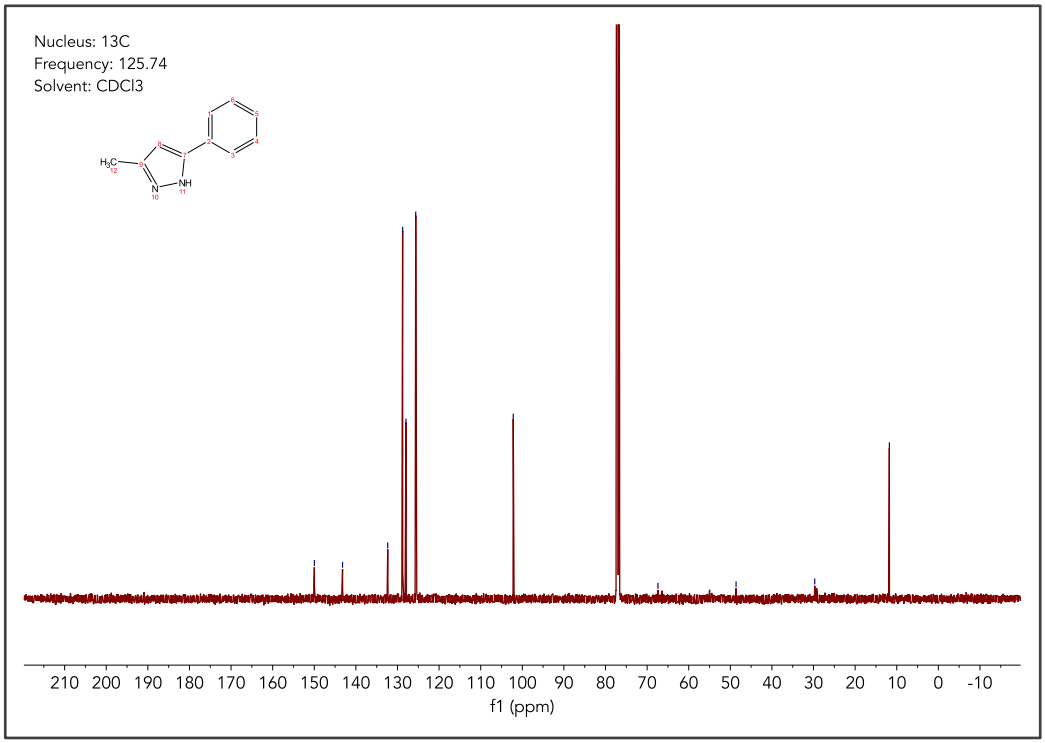

Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
1.07
1.00
1.05
3.26
2.20
2.20
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Nucleus: 13C
Frequency: 125.74 MHz
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

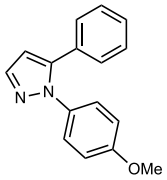
Compound **29**

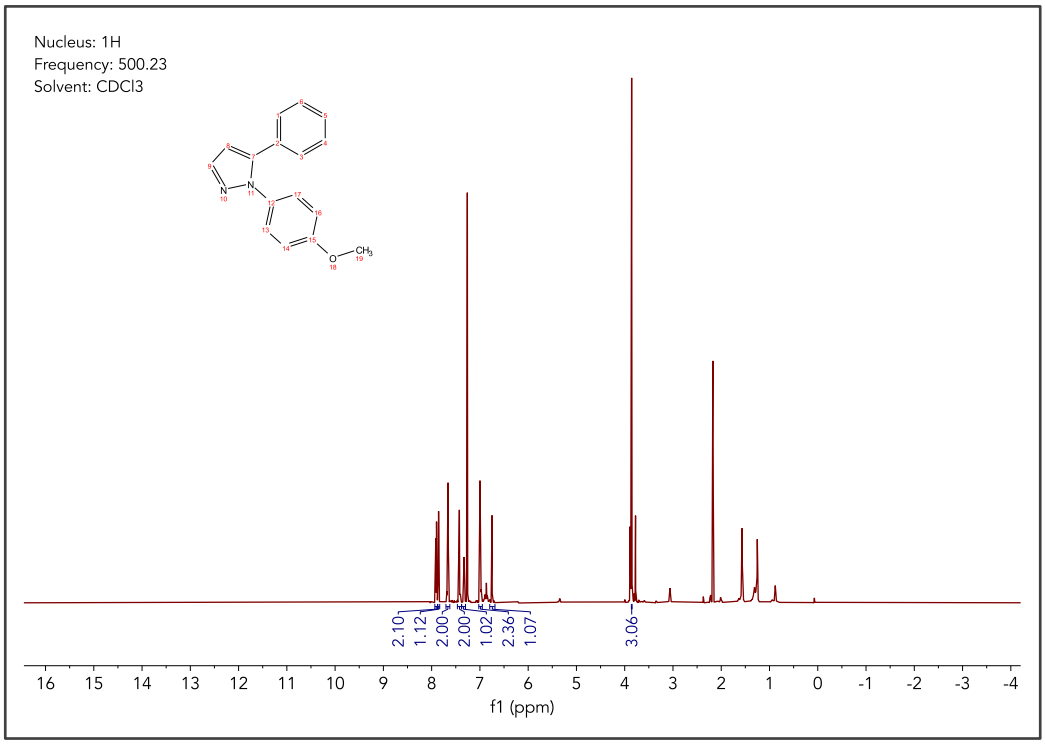

Me
N
NH


Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
1.96
1.97
1.00
1.12
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

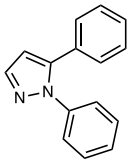

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

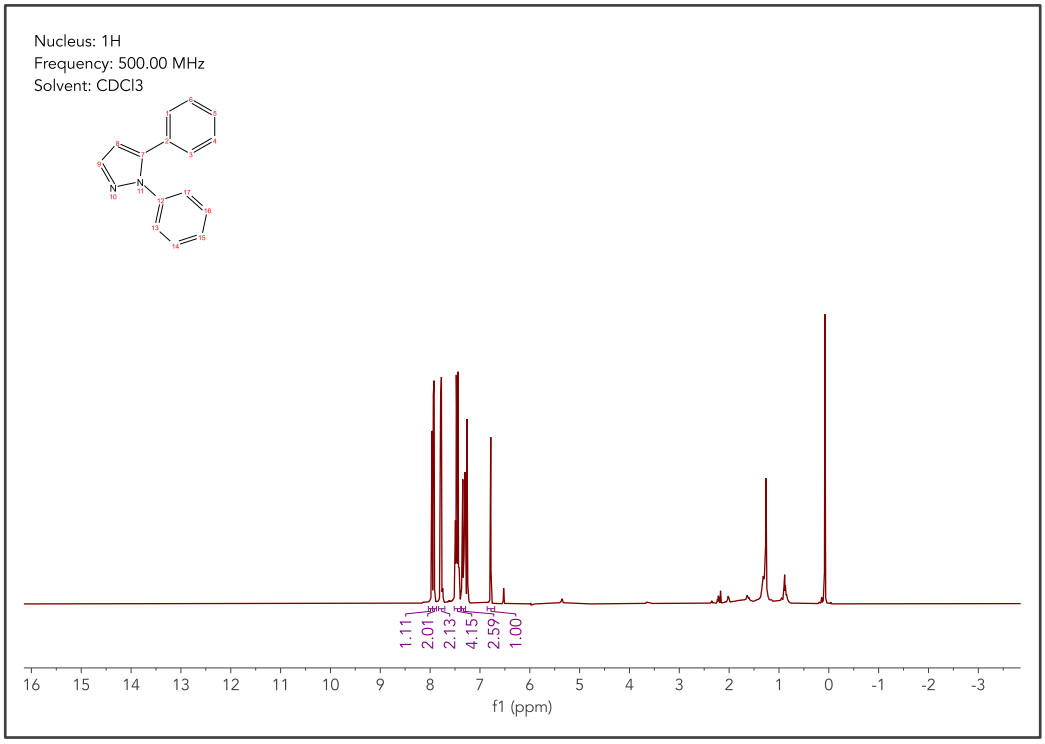
Compound **30**


N
N
OMe

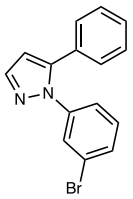

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
2.10
1.12
2.00
2.00
1.02
2.36
1.07
3.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

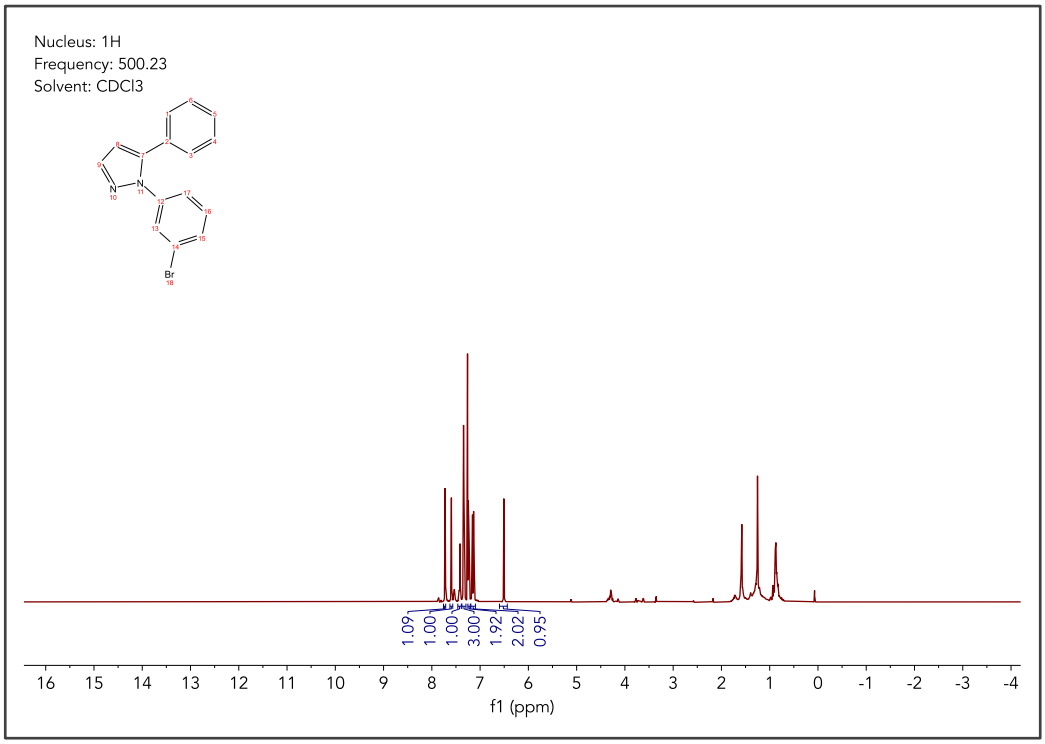
Compound **31**



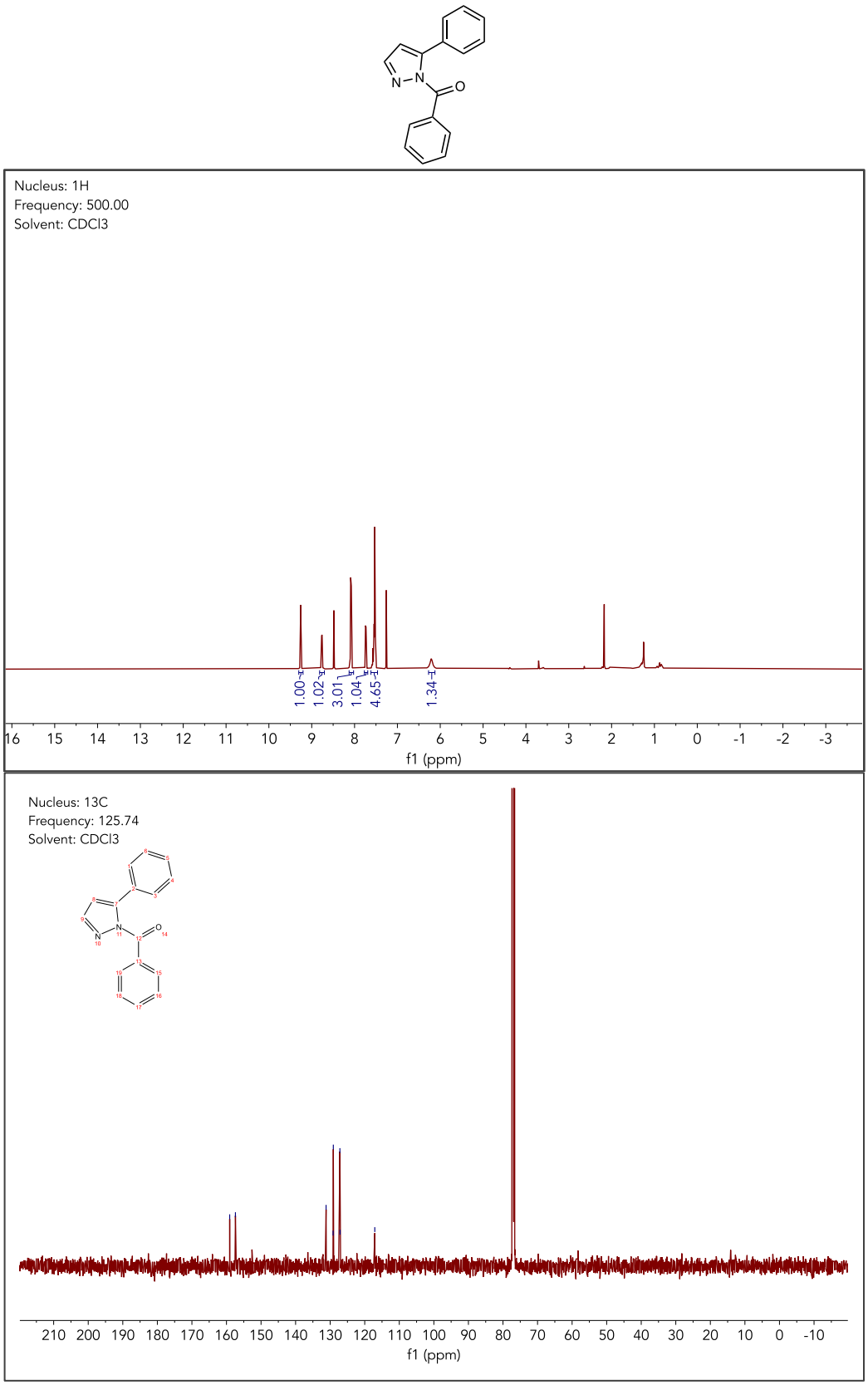

Nucleus: 1H
Frequency: 500.00 MHz
Solvent: CDCl3
1.11
2.01
2.13
4.15
2.59
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

Compound **32a**

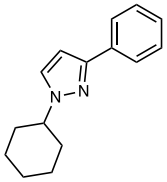


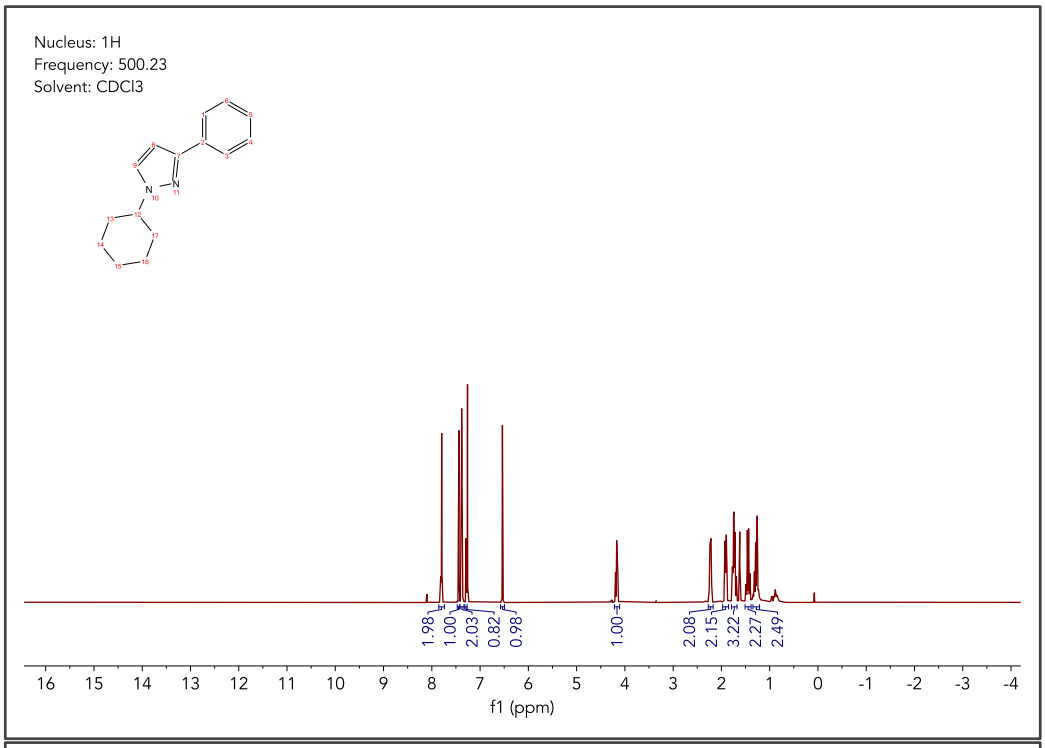


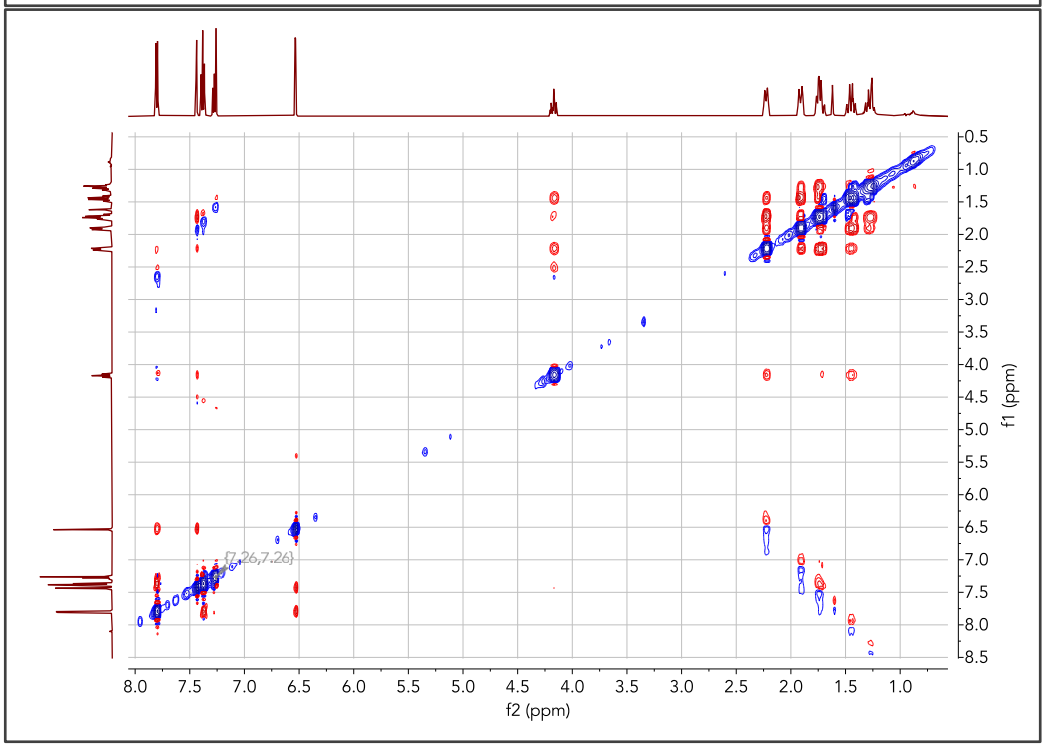
Compound **33**


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
1.00
1.02
3.01
1.04
4.65
1.34
f1 (ppm)
Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
f1 (ppm)

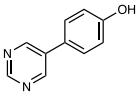
Compound **34**

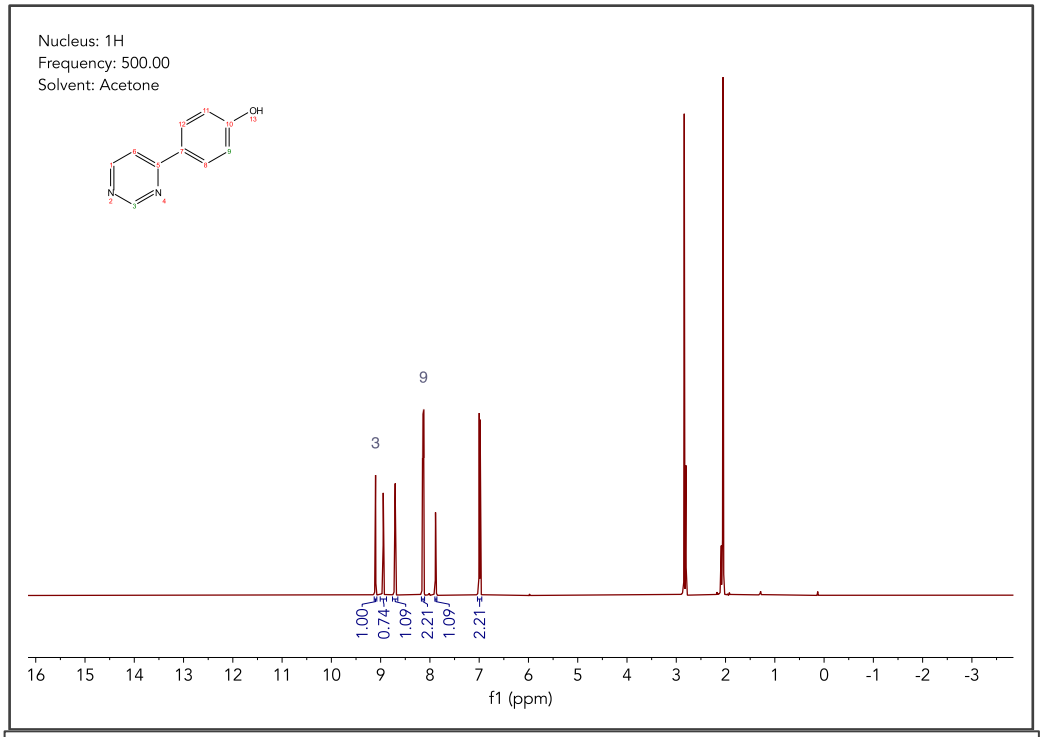


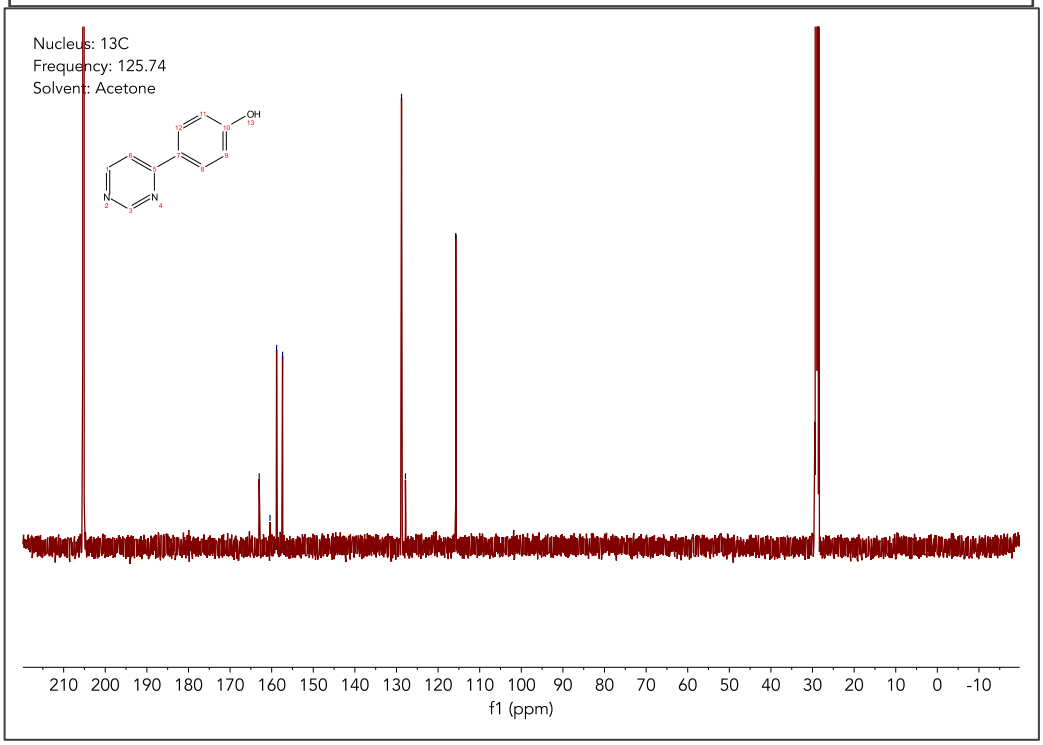

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
1.98
1.00
2.03
0.82
0.98
1.00
2.08
2.15
3.22
2.27
2.49
f1 (ppm)


f1 (ppm)
f2 (ppm)

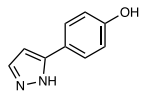
Compound **S40**

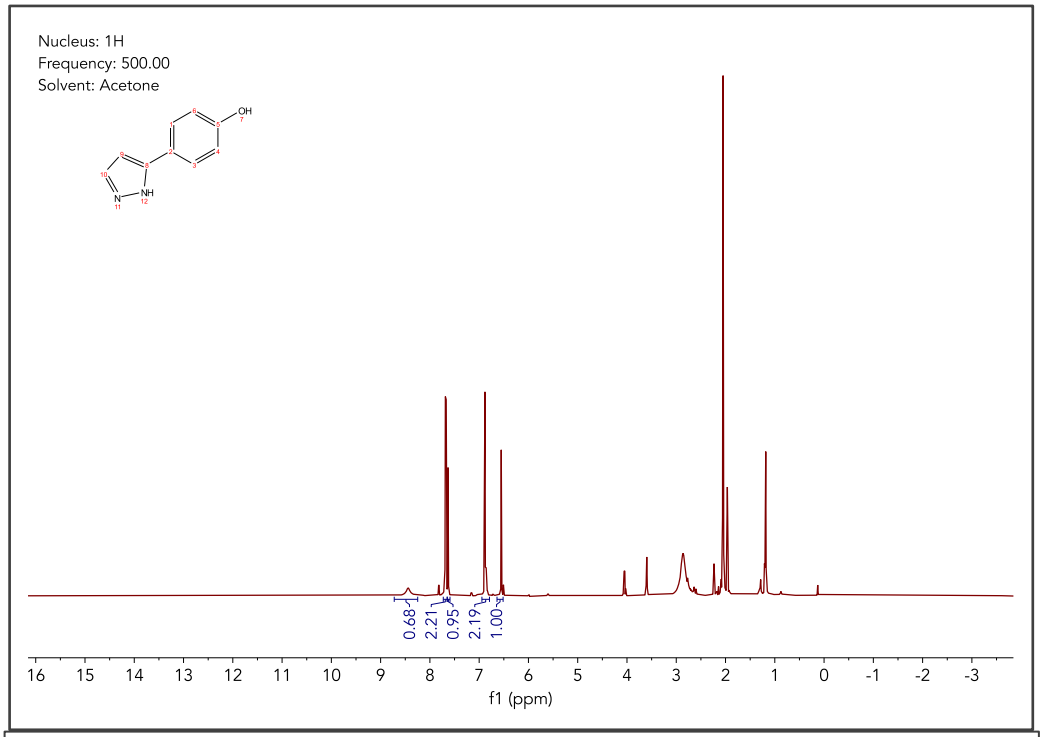


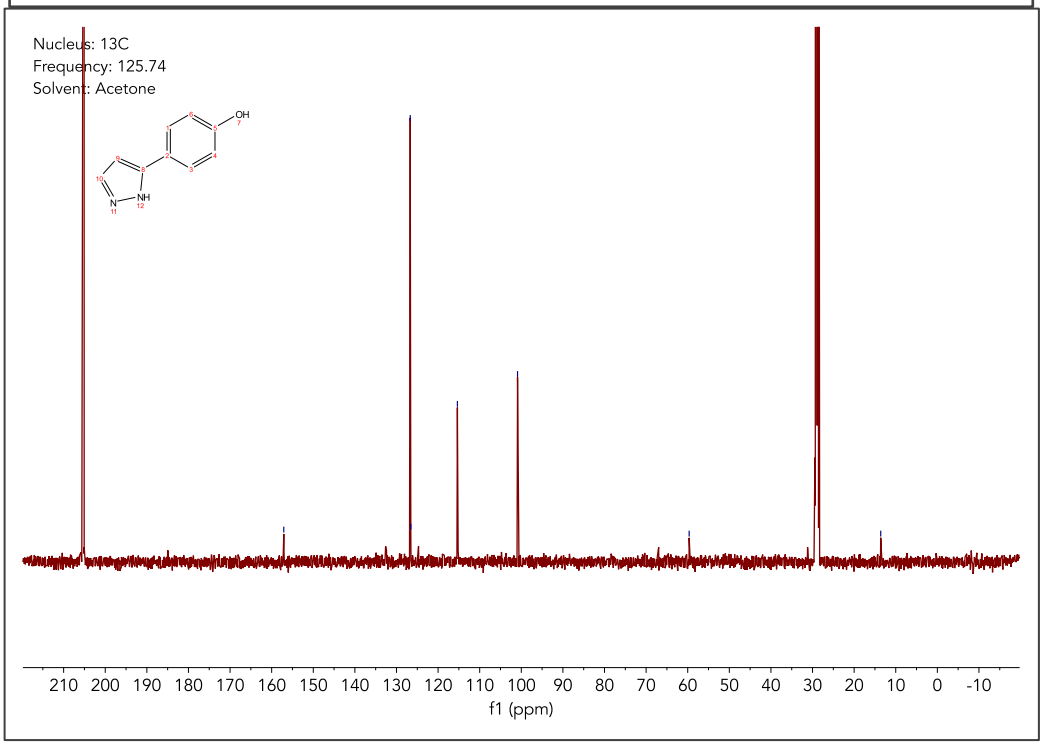




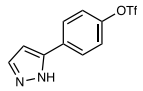
Compound **35**

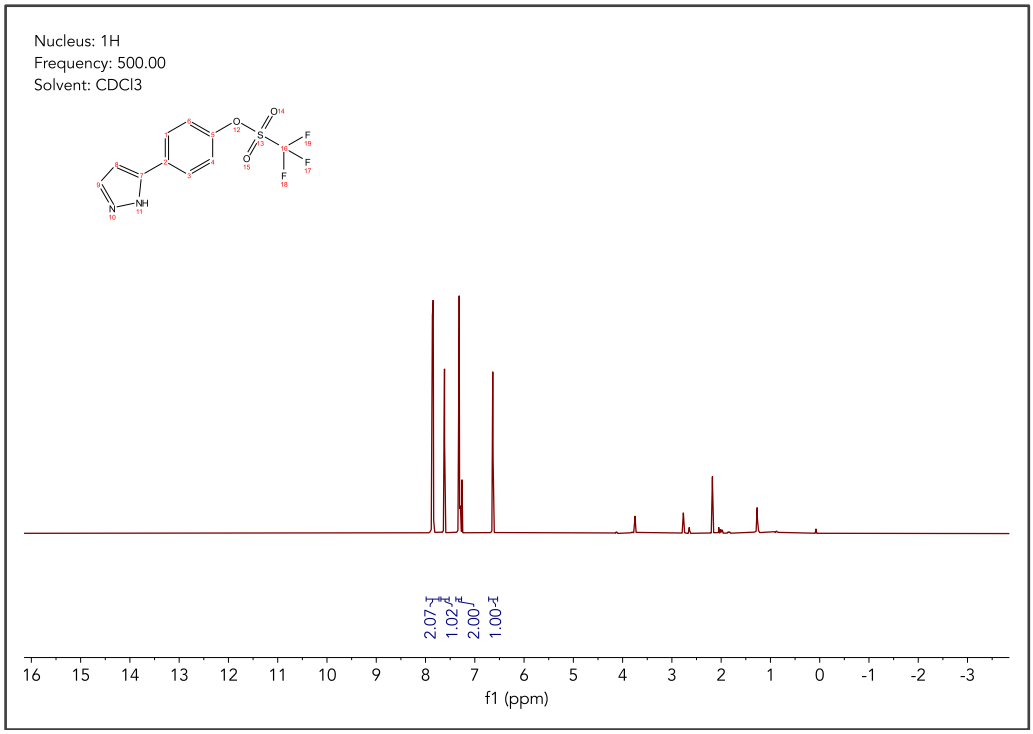

OH
NH
N

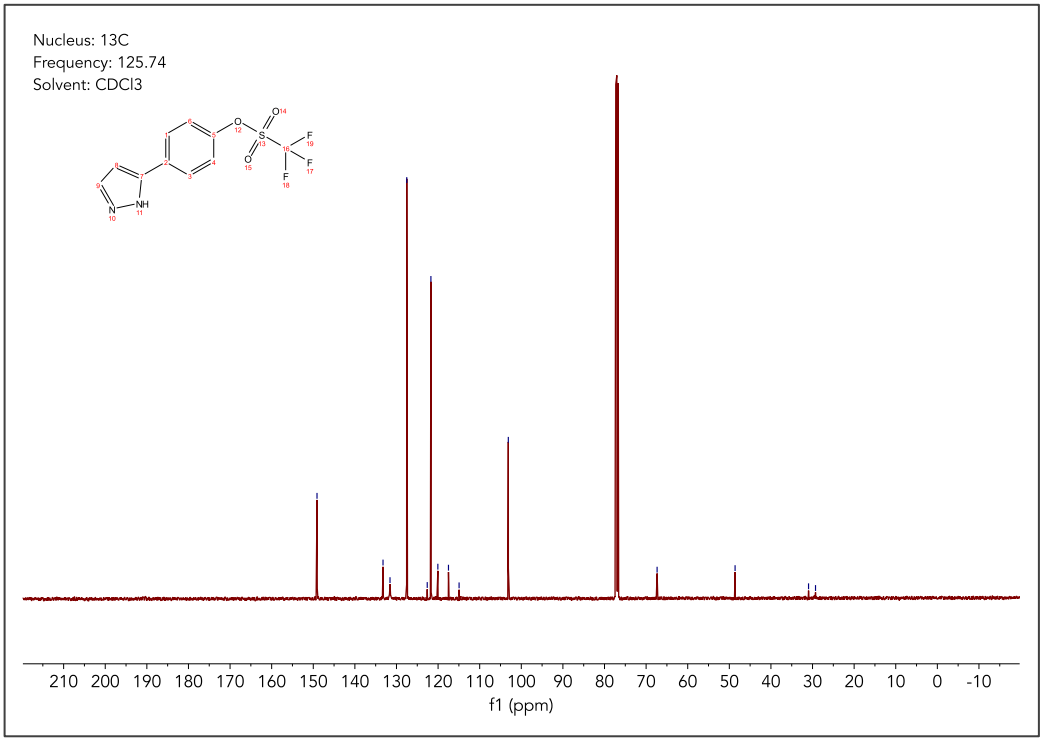

Nucleus: 1H
Frequency: 500.00
Solvent: Acetone
0.68
2.21
0.95
2.19
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: Acetone
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

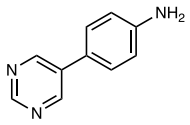
Compound **36**

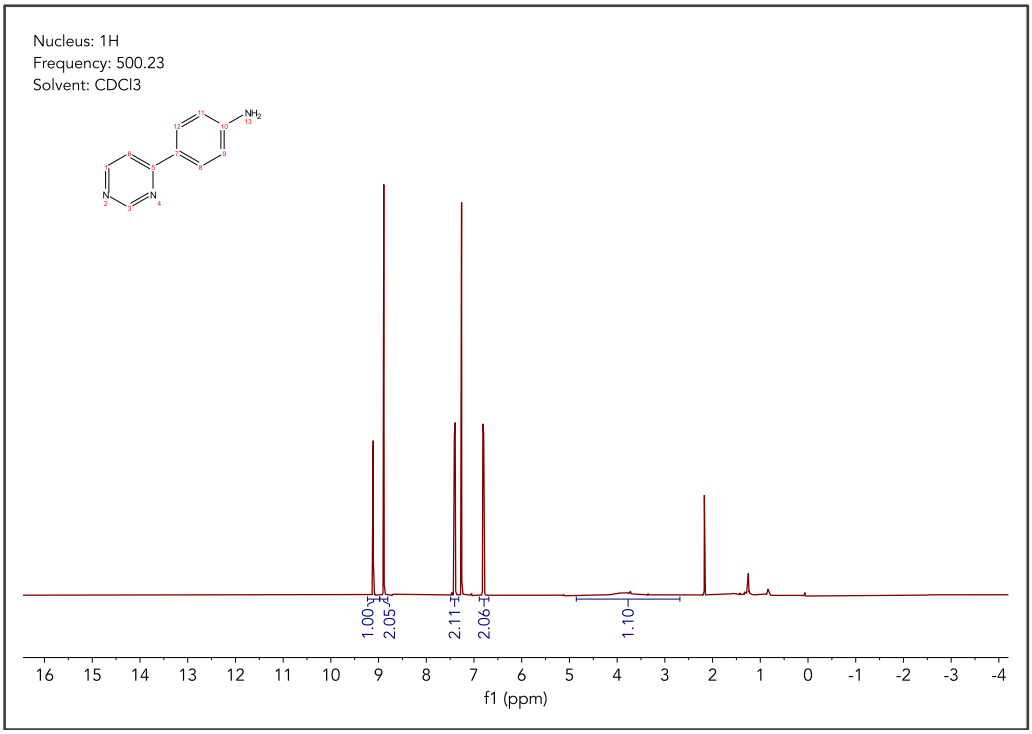

OTf
NH
N


Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
2.07
1.02
2.00
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

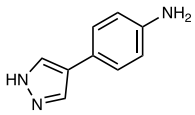

Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

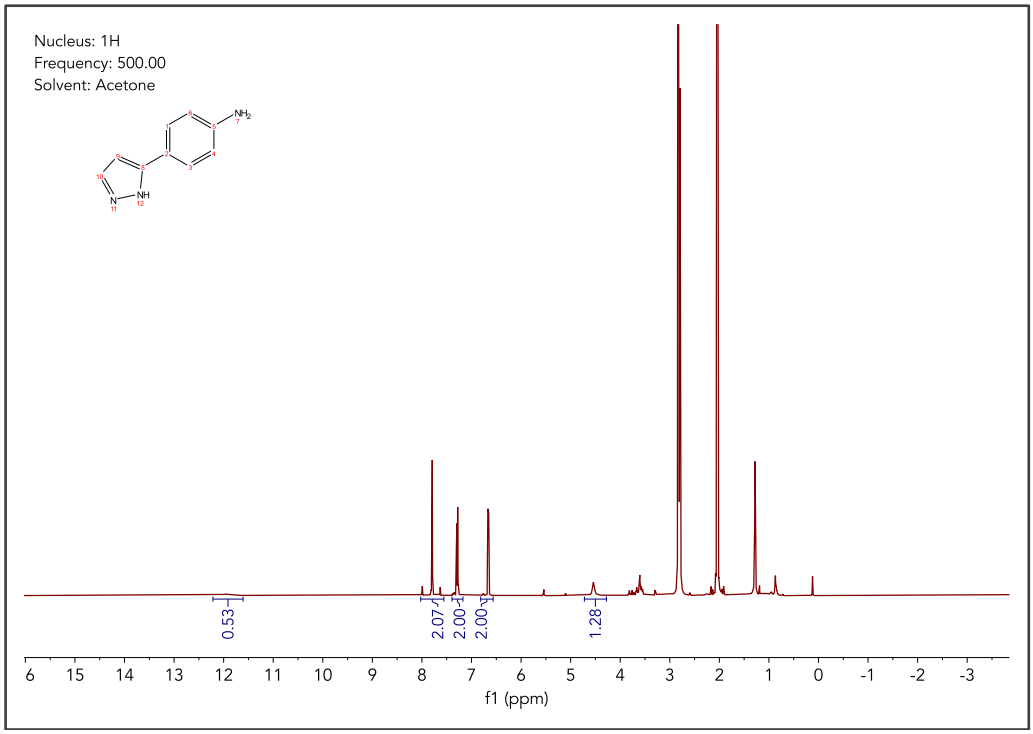
Compound **S41**



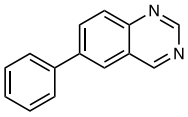


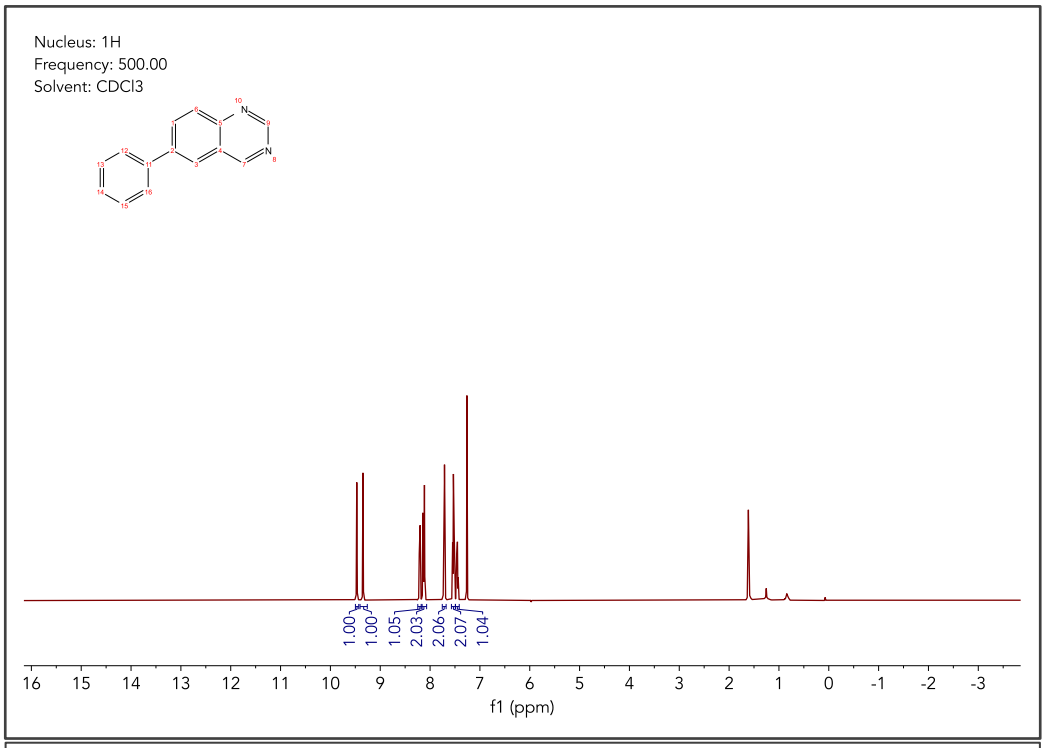
Compound **37**

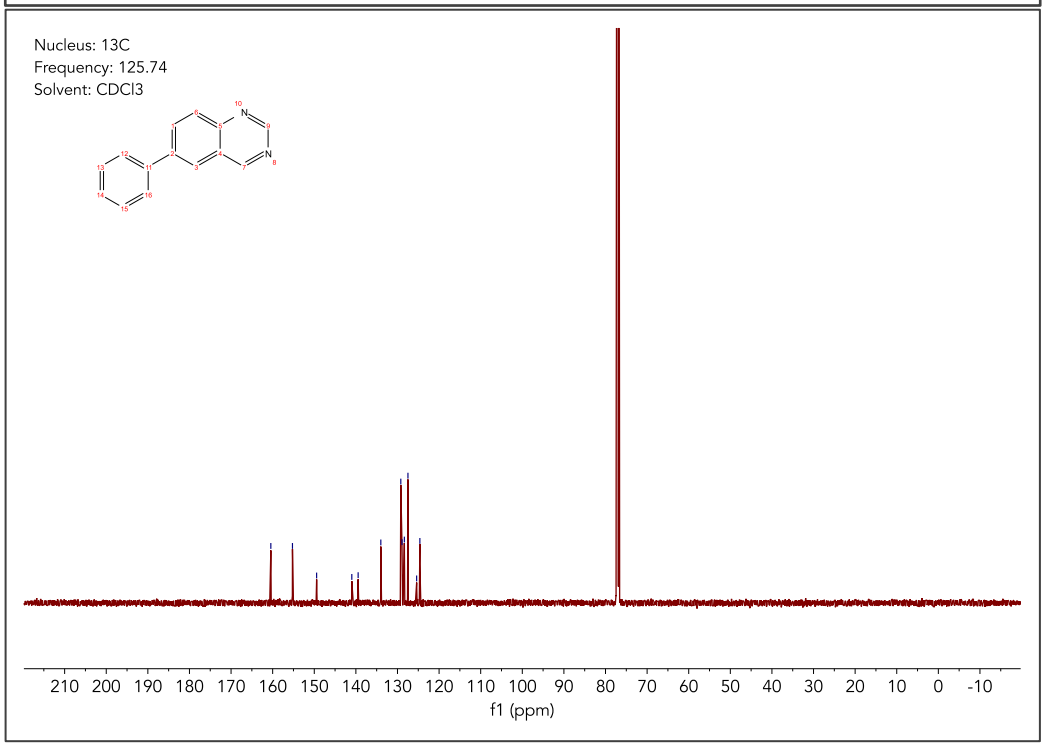

NH2
HN
N


Nucleus: 1H
Frequency: 500.00
Solvent: Acetone
0.53
2.07
2.00
2.00
1.28
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

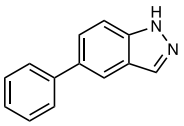
Compound **S42**

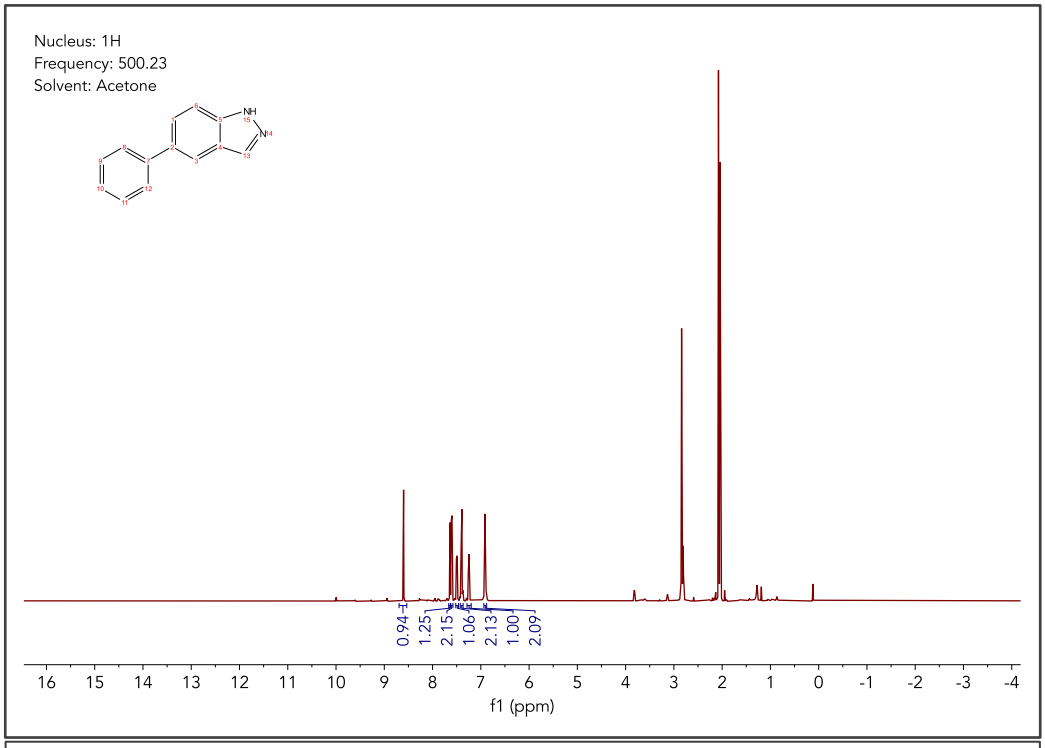


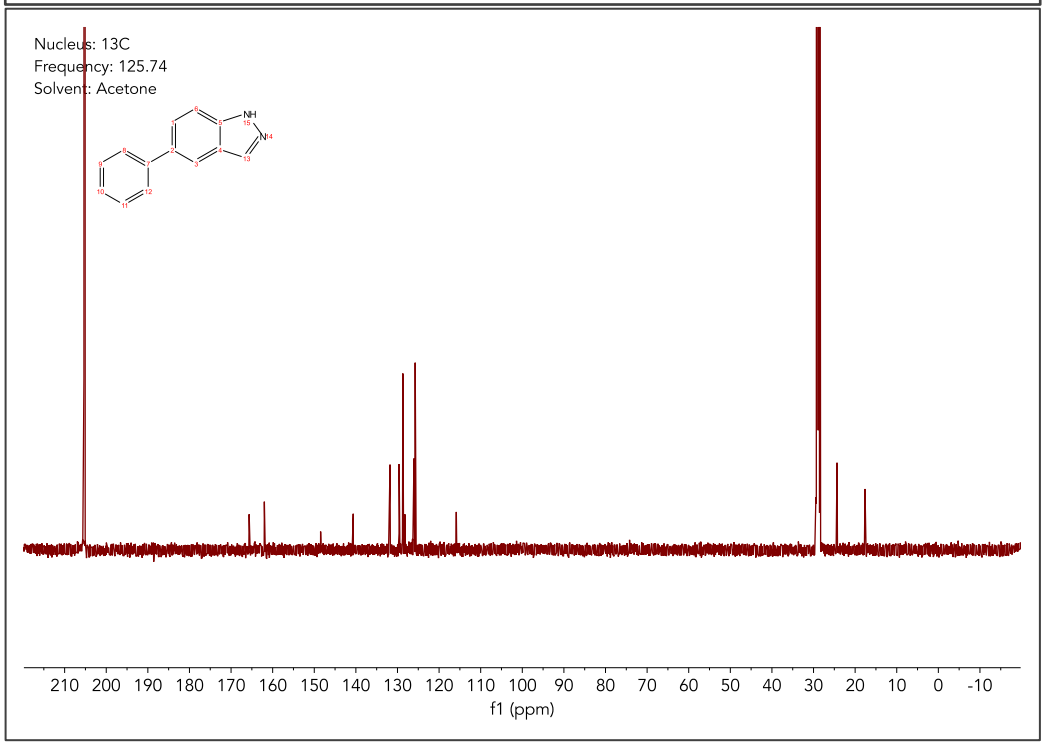




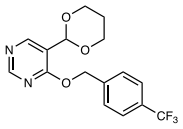
Compound **38**

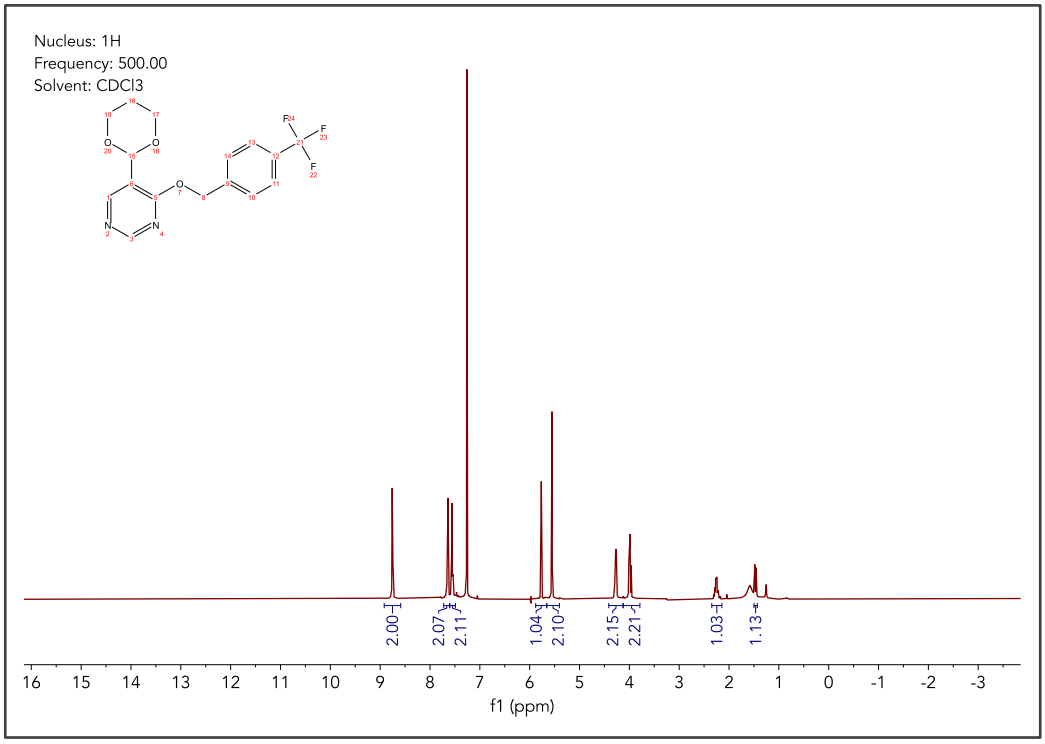



Nucleus: 1H
Frequency: 500.23
Solvent: Acetone
0.94
1.25
2.15
1.06
2.13
1.00
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

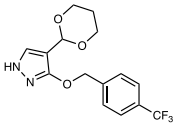

Nucleus: 13C
Frequency: 125.74
Solvent: Acetone
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

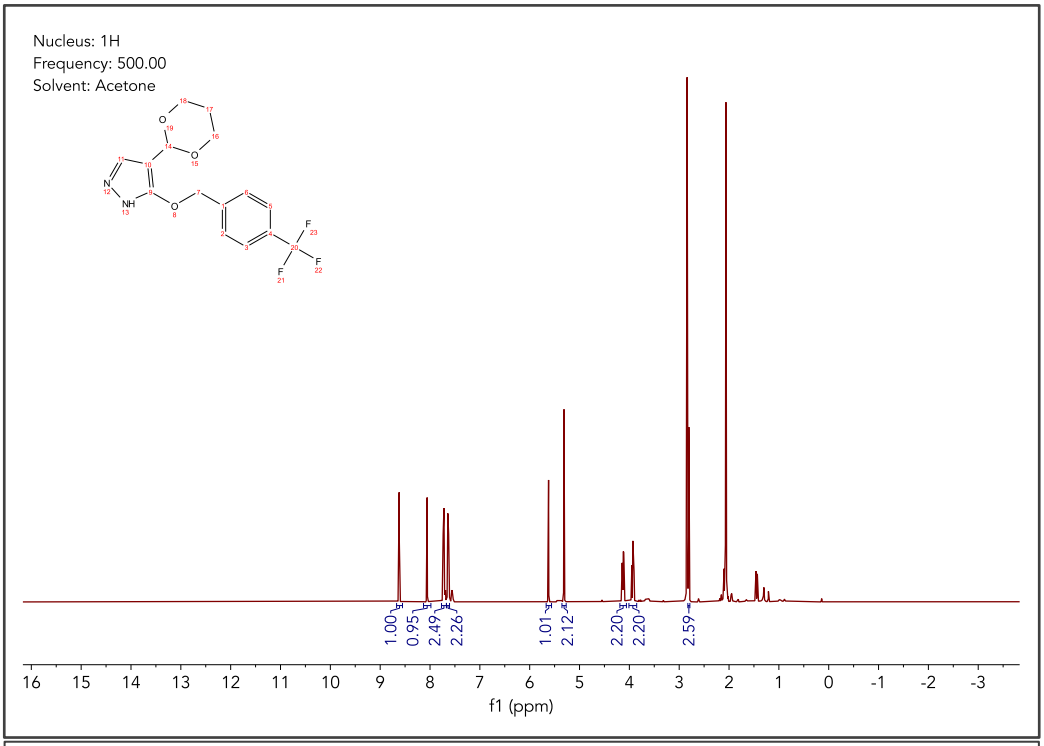
Compound **39**

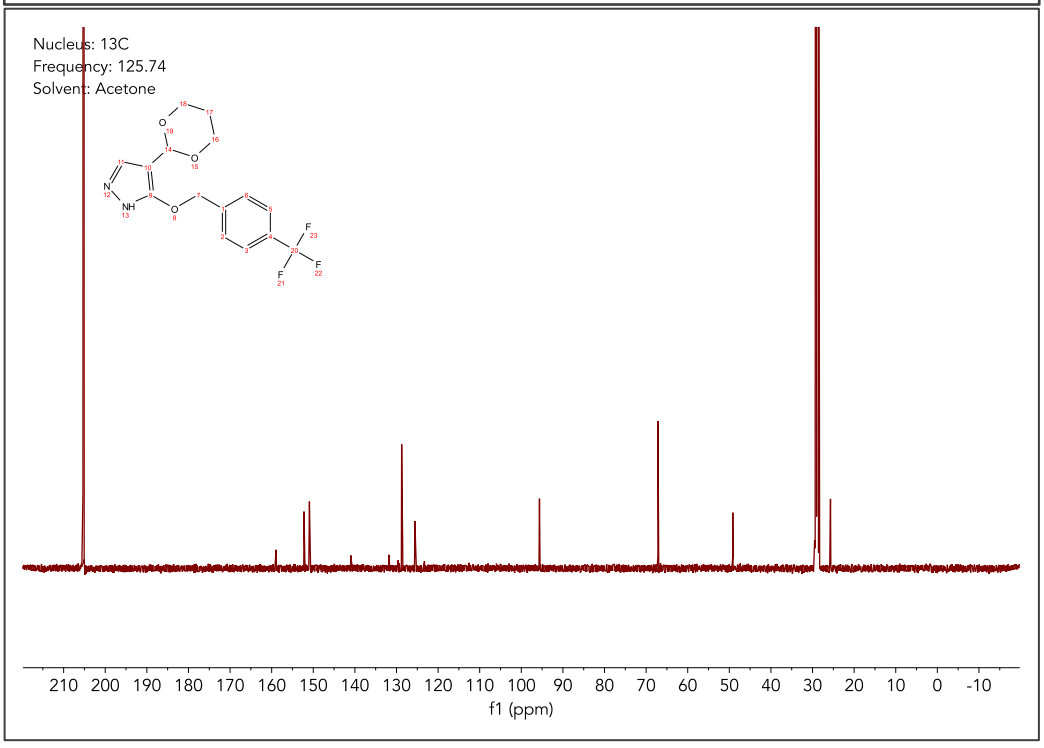



Nucleus: 1H
Frequency: 500.00
Solvent: CDCl3
2.00
2.07
2.11
1.04
2.10
2.15
2.21
1.03
1.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

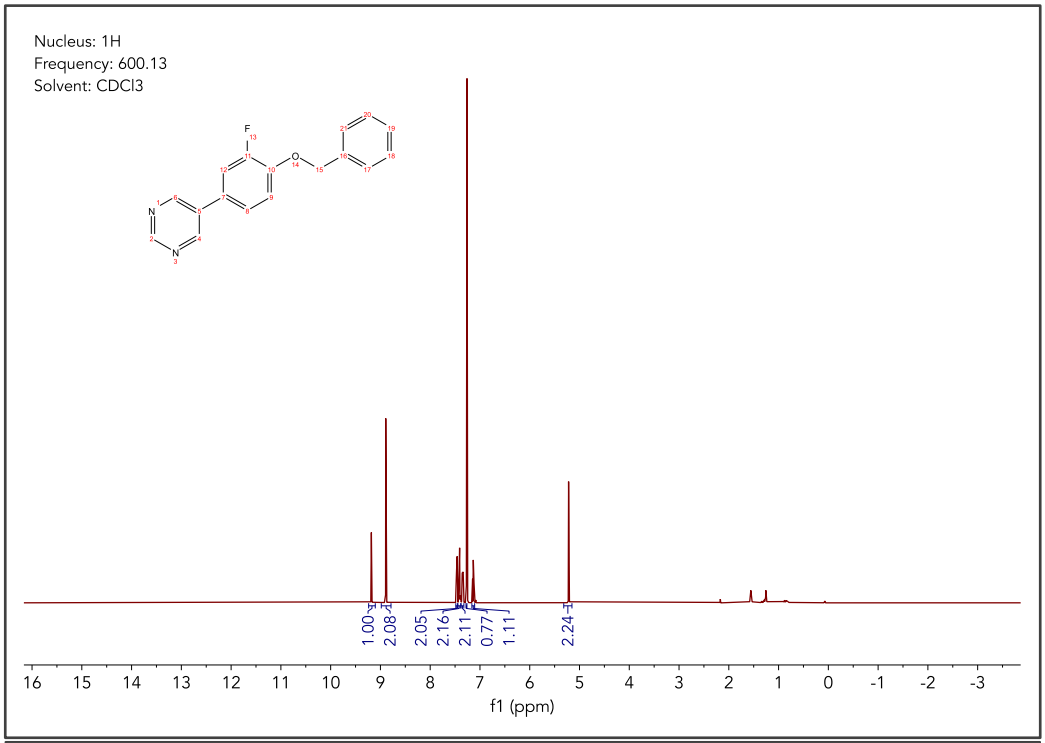
Compound **S43**

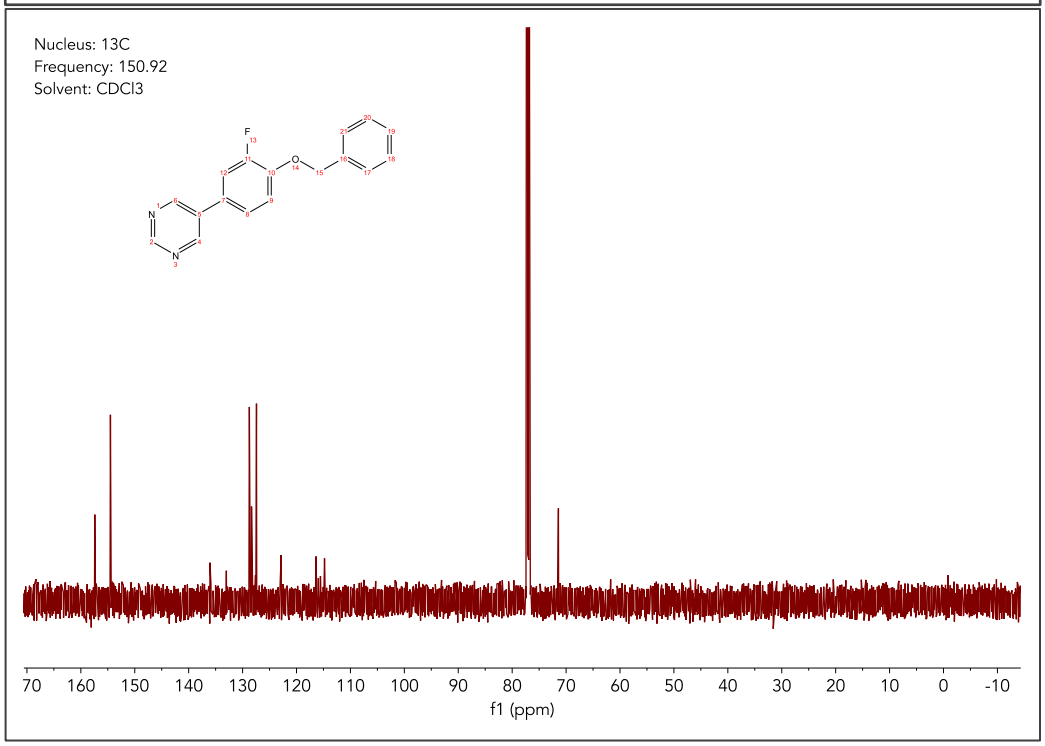




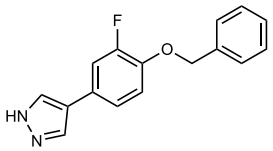


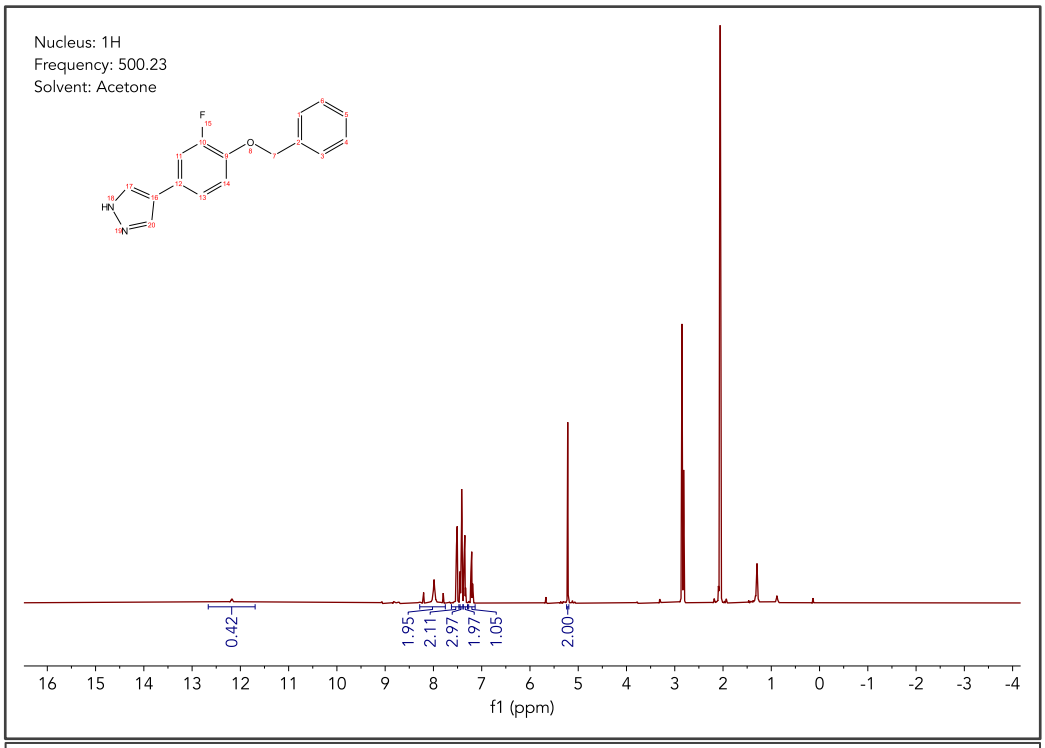
Compound **40**

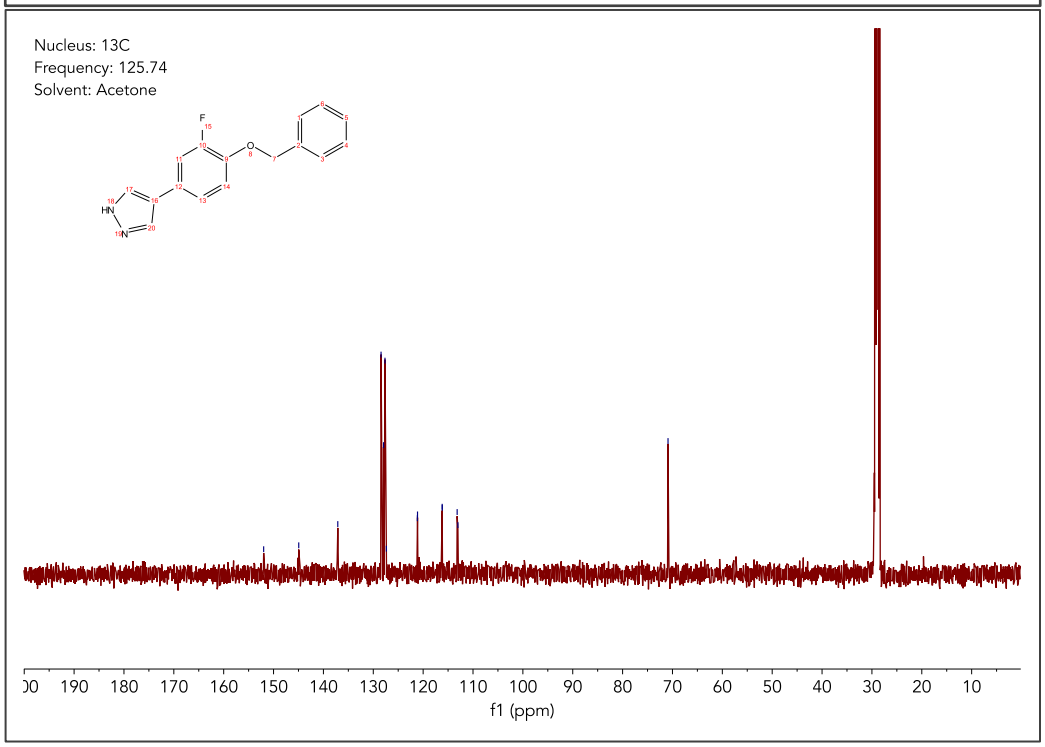

Nucleus: 1H
Frequency: 600.13
Solvent: CDCl3
1.00
2.08
2.05
2.16
2.11
0.77
1.11
2.24
f1 (ppm)


Nucleus: 13C
Frequency: 150.92
Solvent: CDCl3
f1 (ppm)

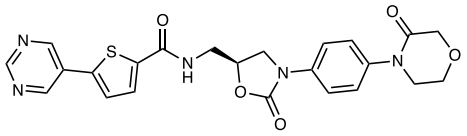
Compound **S44**

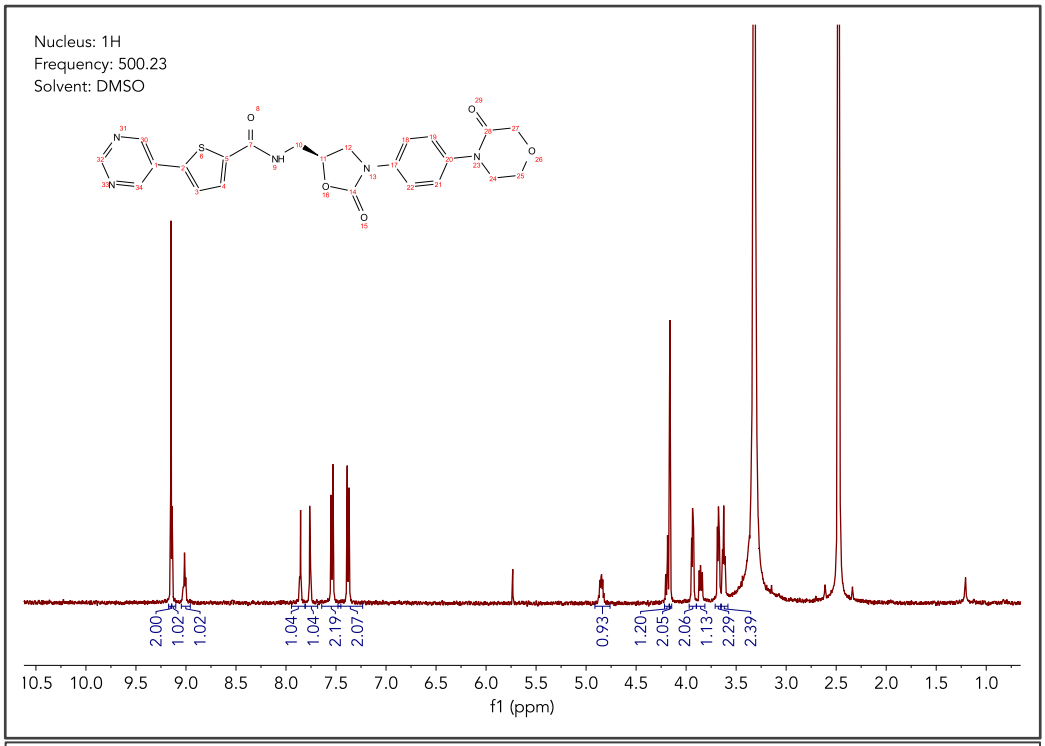


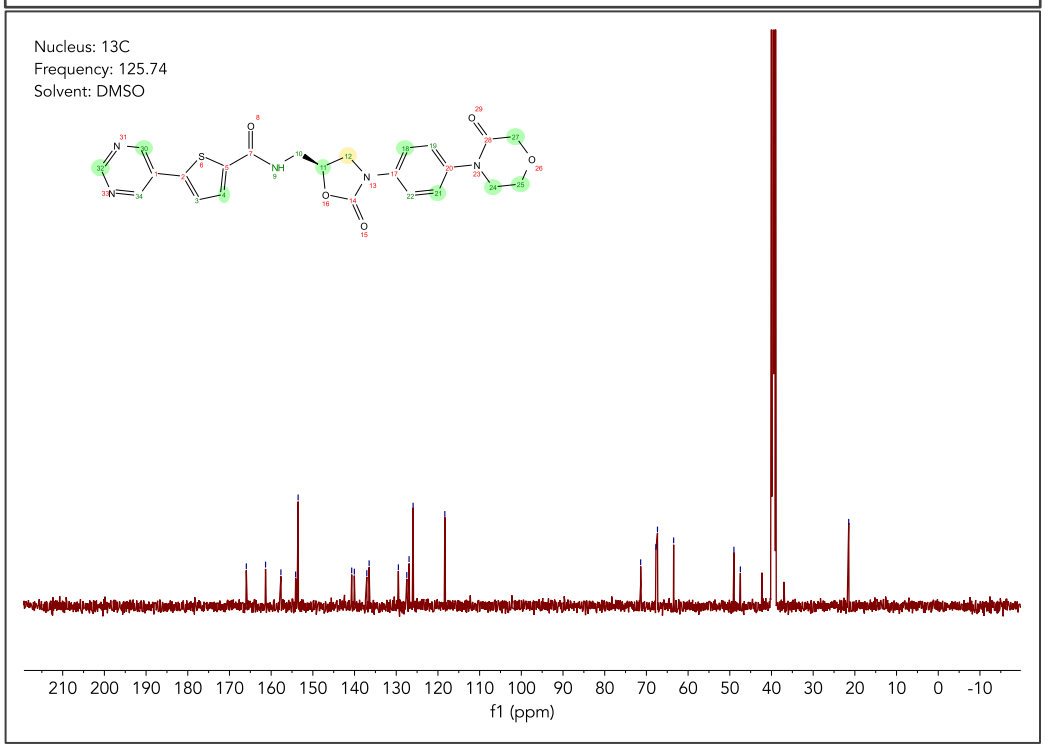




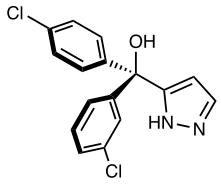
Compound **42**

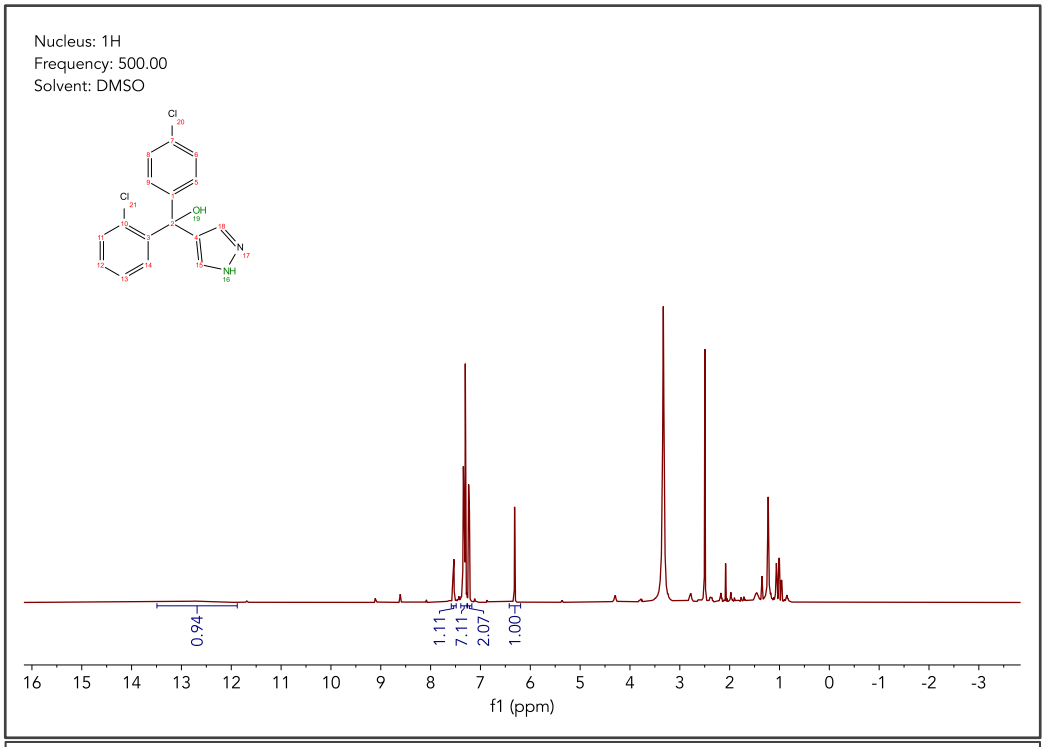


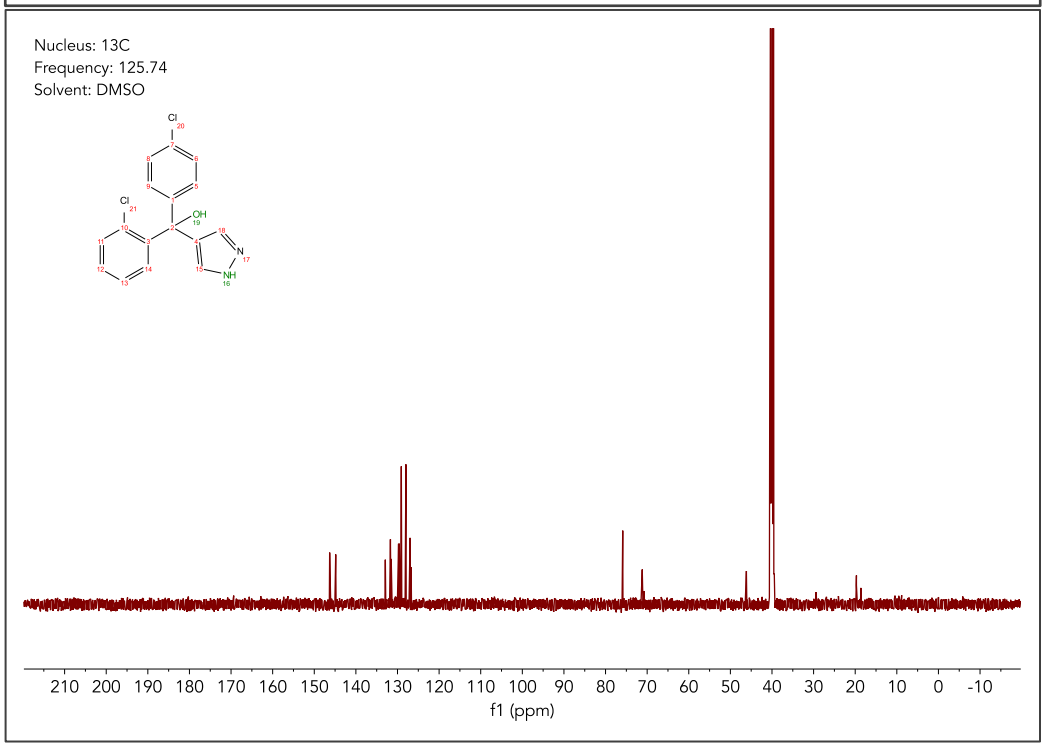

Nucleus: 1H
Frequency: 500.23
Solvent: DMSO
2.00
1.02
1.02
1.04
1.04
2.19
2.07
0.93
1.20
2.05
2.06
1.13
2.29
2.39
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: DMSO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

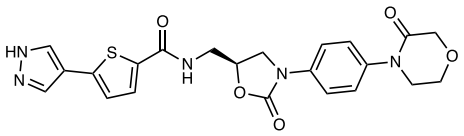
Compound **S45**

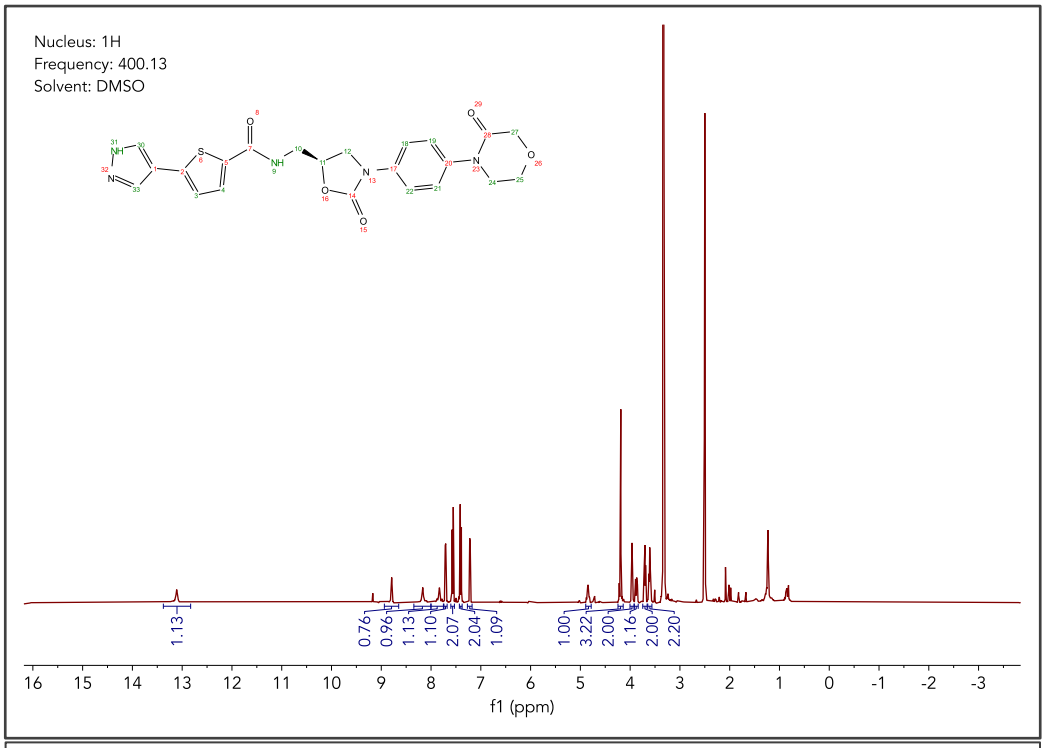


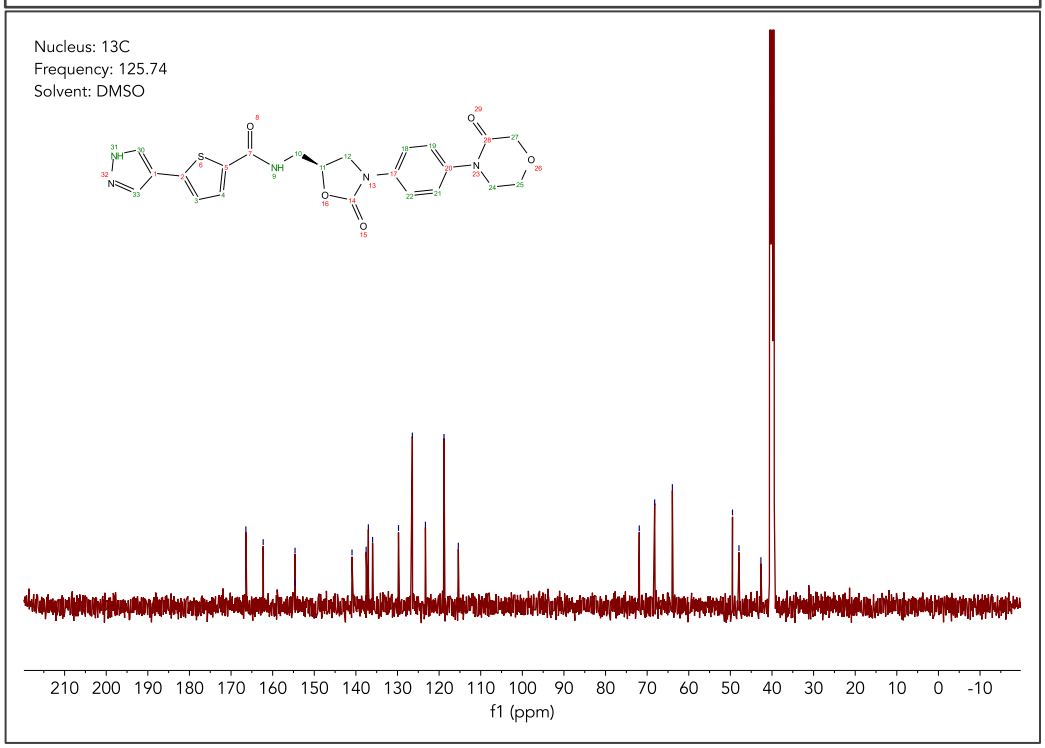




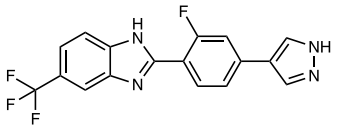
Compound **S46**

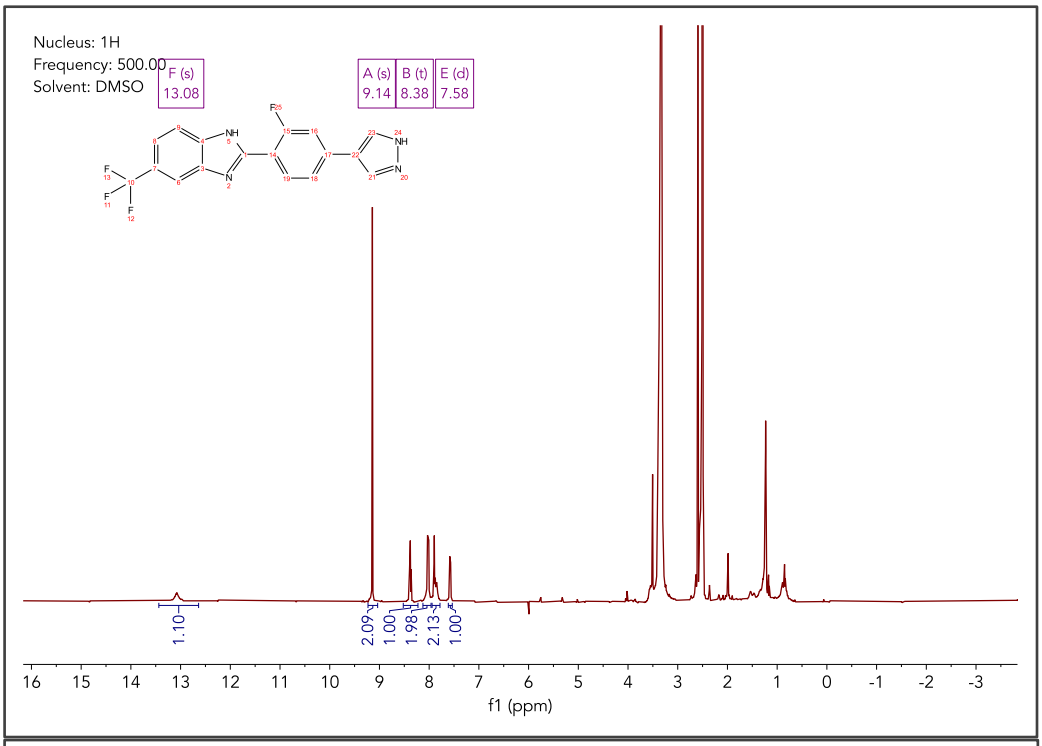


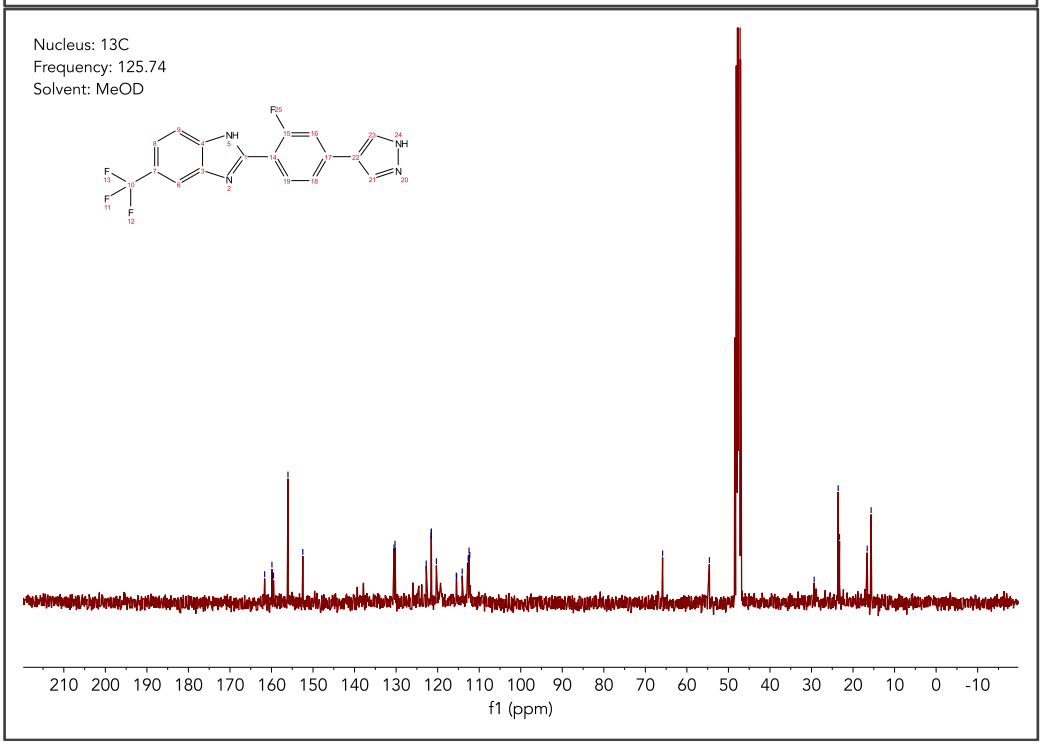




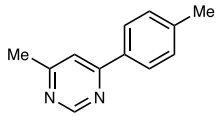
Compound **S47**

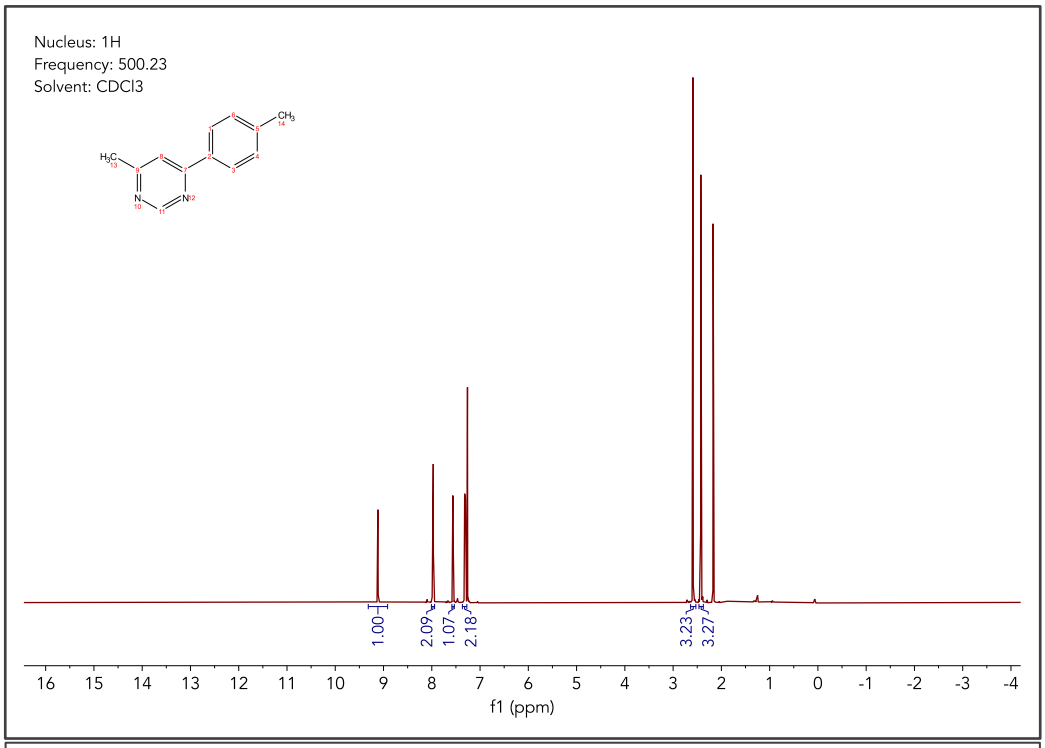


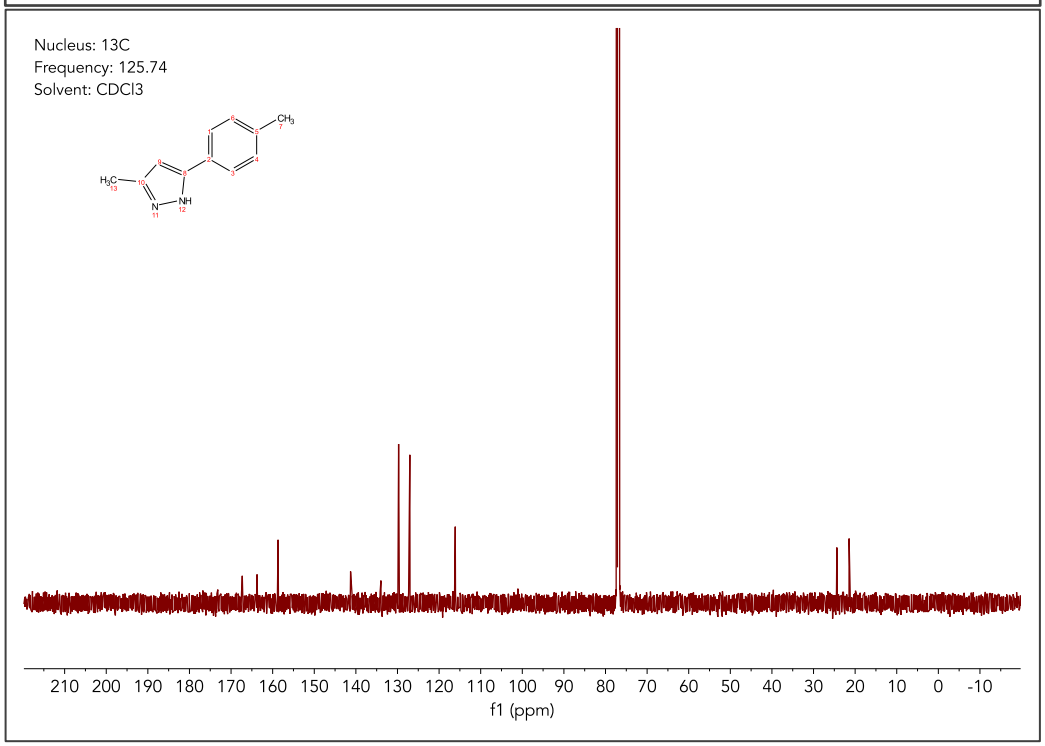




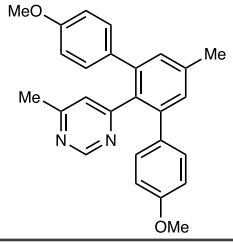
Compound **44**

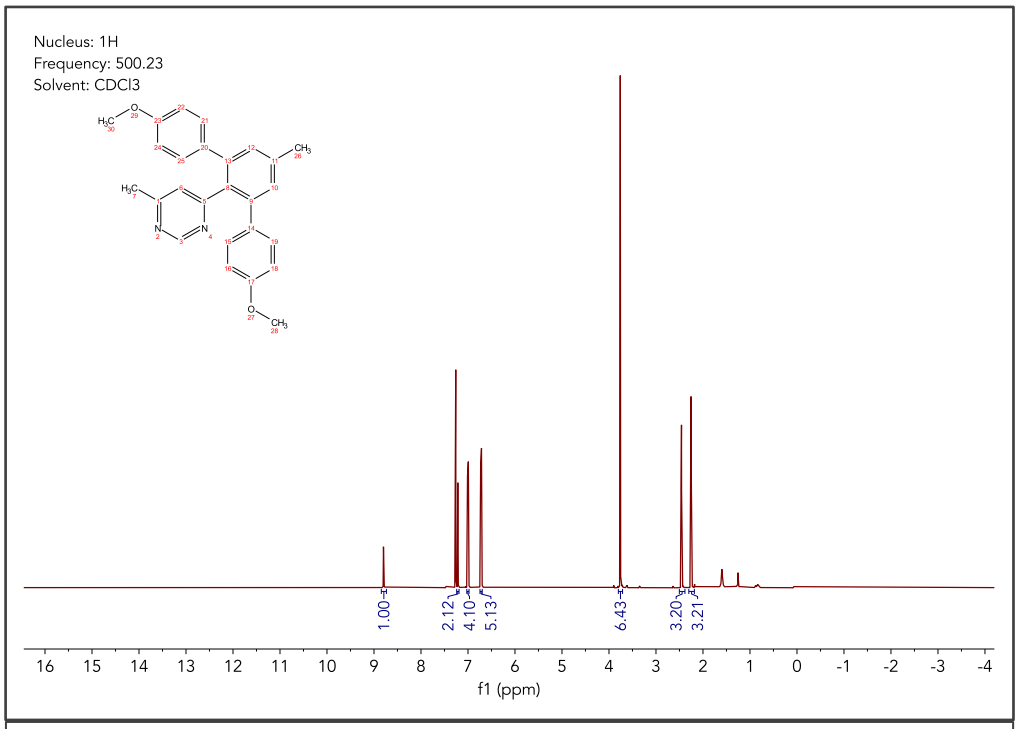

Me
Me
N
N

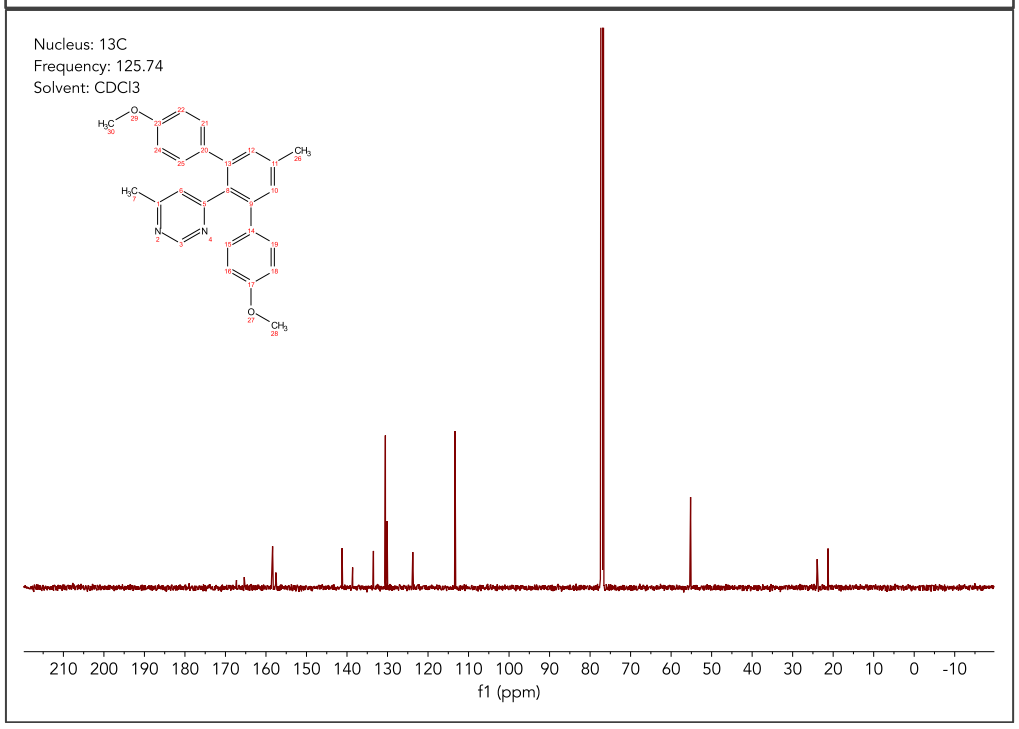

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
1.00
2.09
1.07
2.18
3.23
3.27
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

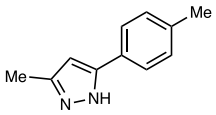
Compound **45**

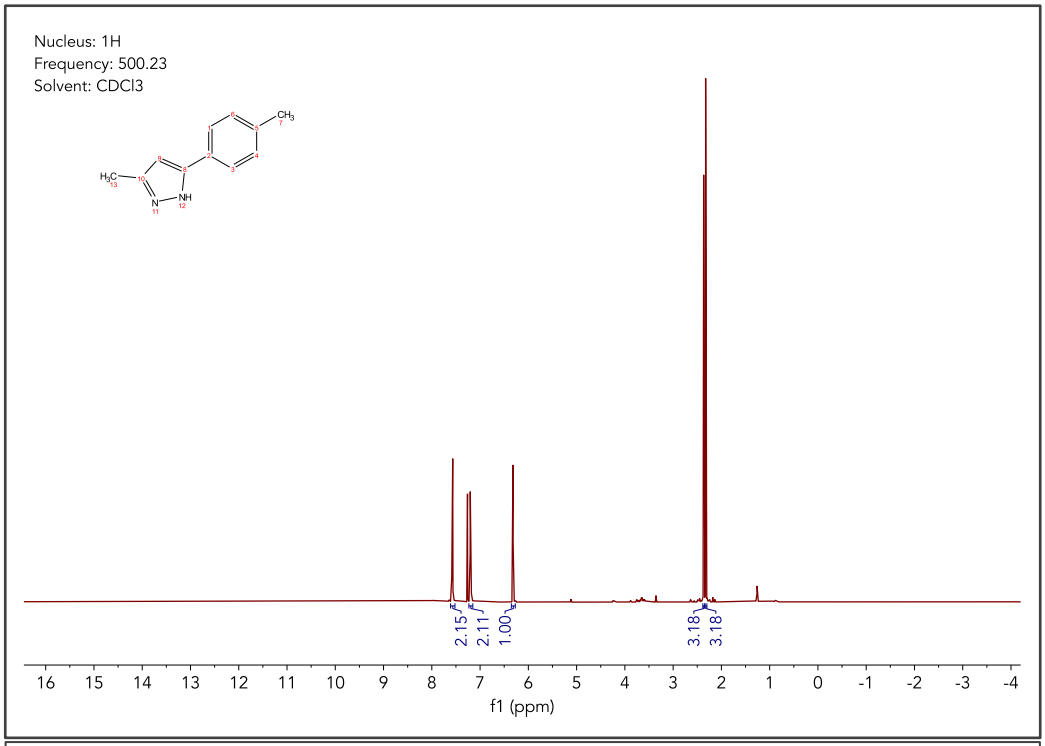

MeO
Me
Me
N
N
OMe

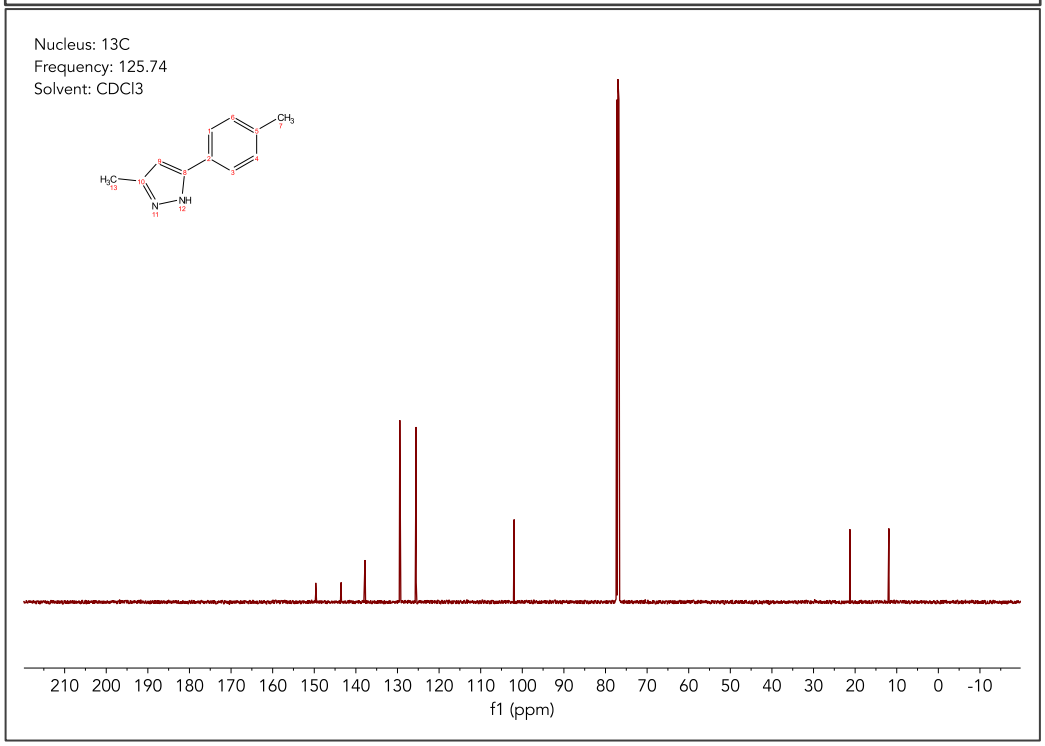

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
1.00
2.12
4.10
5.13
6.43
3.20
3.21
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

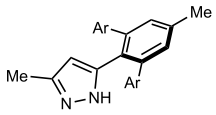
Compound **S48**

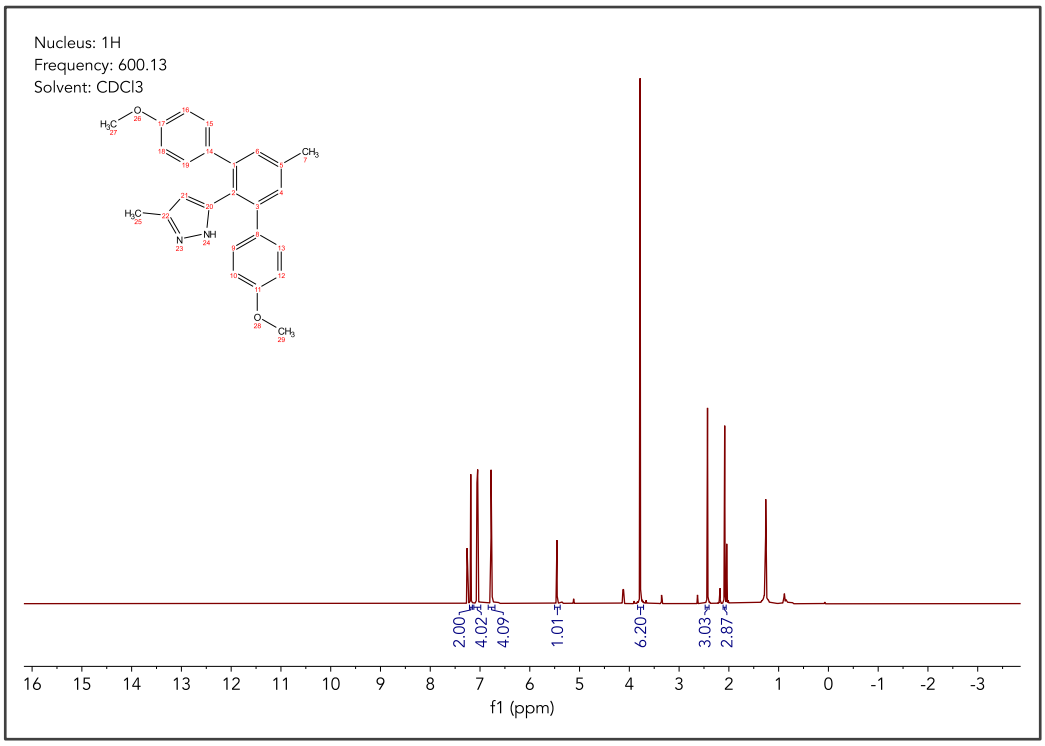


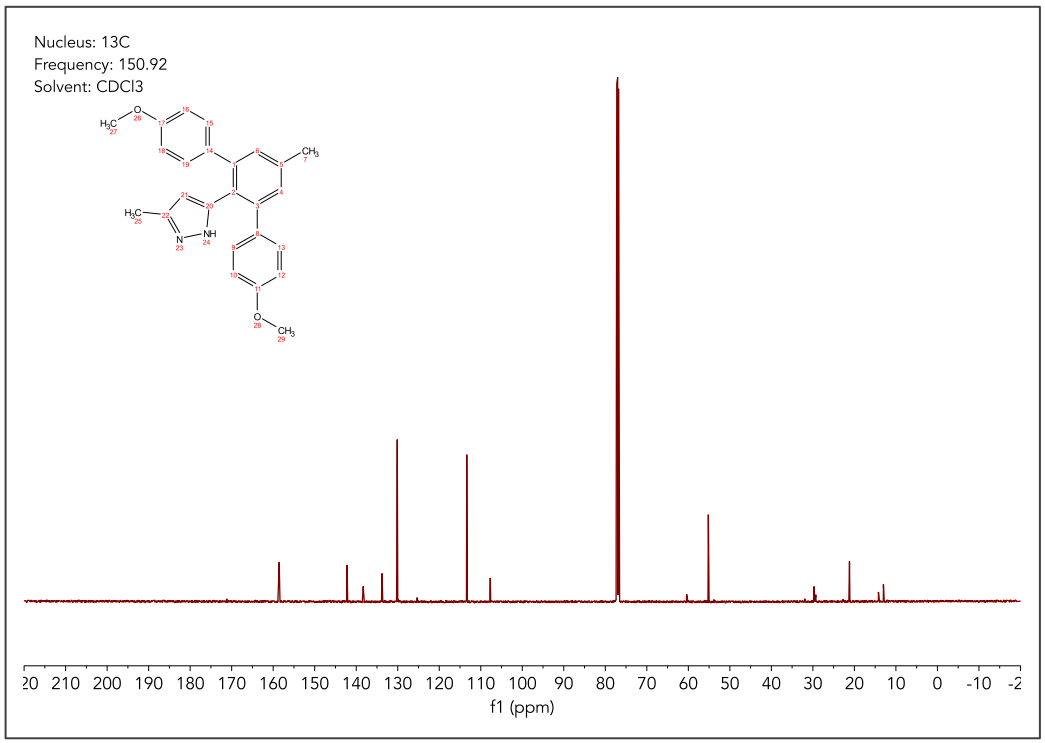




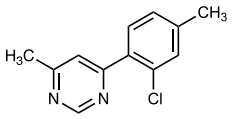
Compound **46**

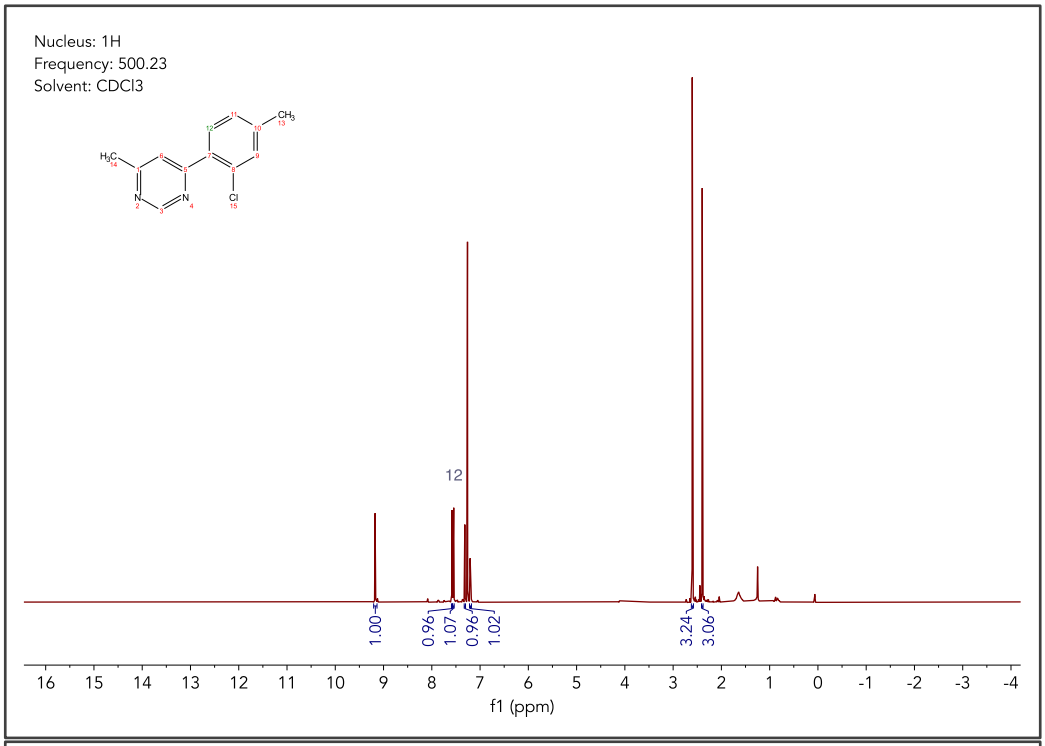

Me
Ar
Me
Ar
N
NH

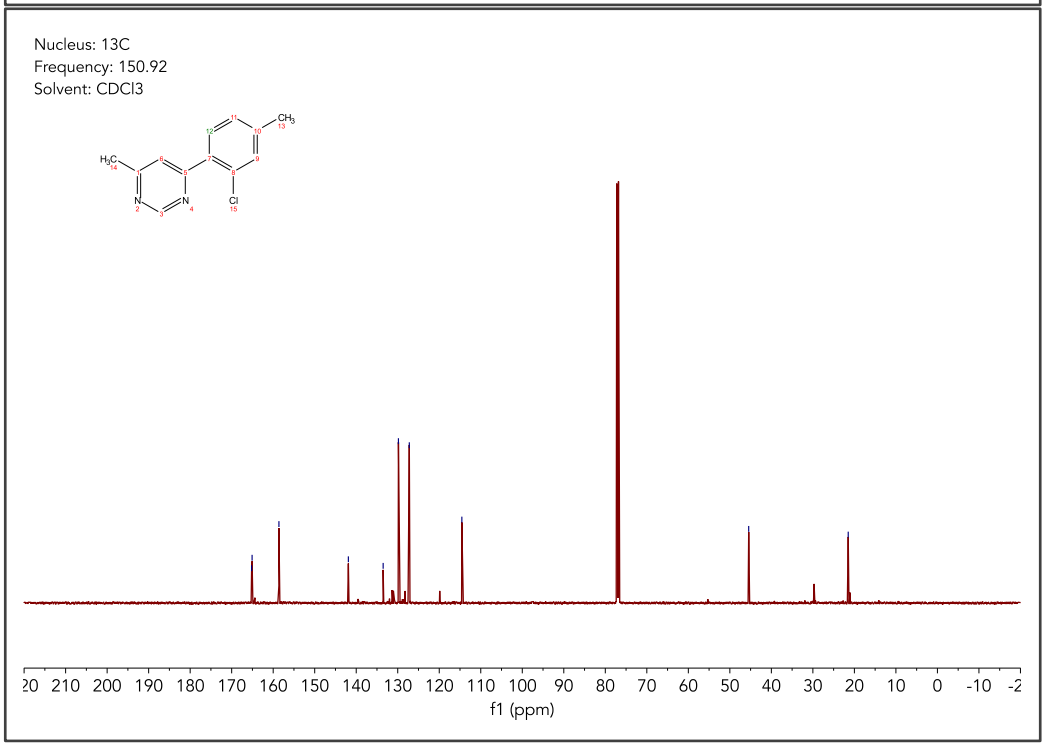

Nucleus: 1H
Frequency: 600.13
Solvent: CDCl3
2.00
4.02
4.09
1.01
6.20
3.03
2.87
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


Nucleus: 13C
Frequency: 150.92
Solvent: CDCl3
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

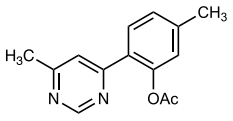
Compound **47**

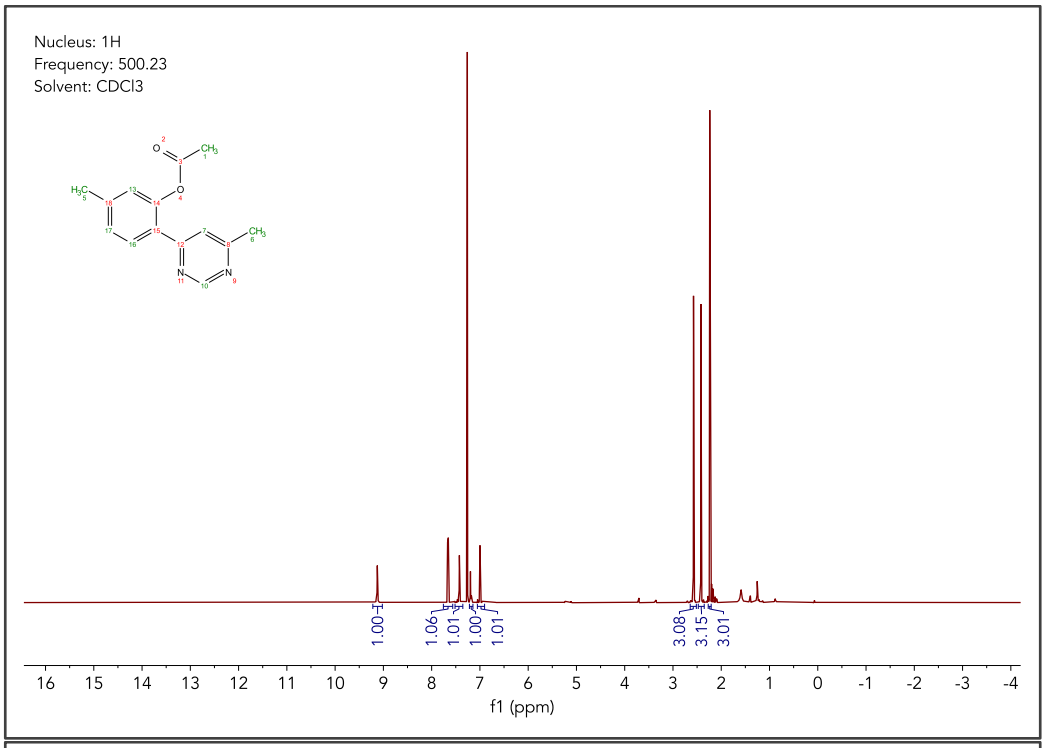

CH3
H3C
N
N
Cl

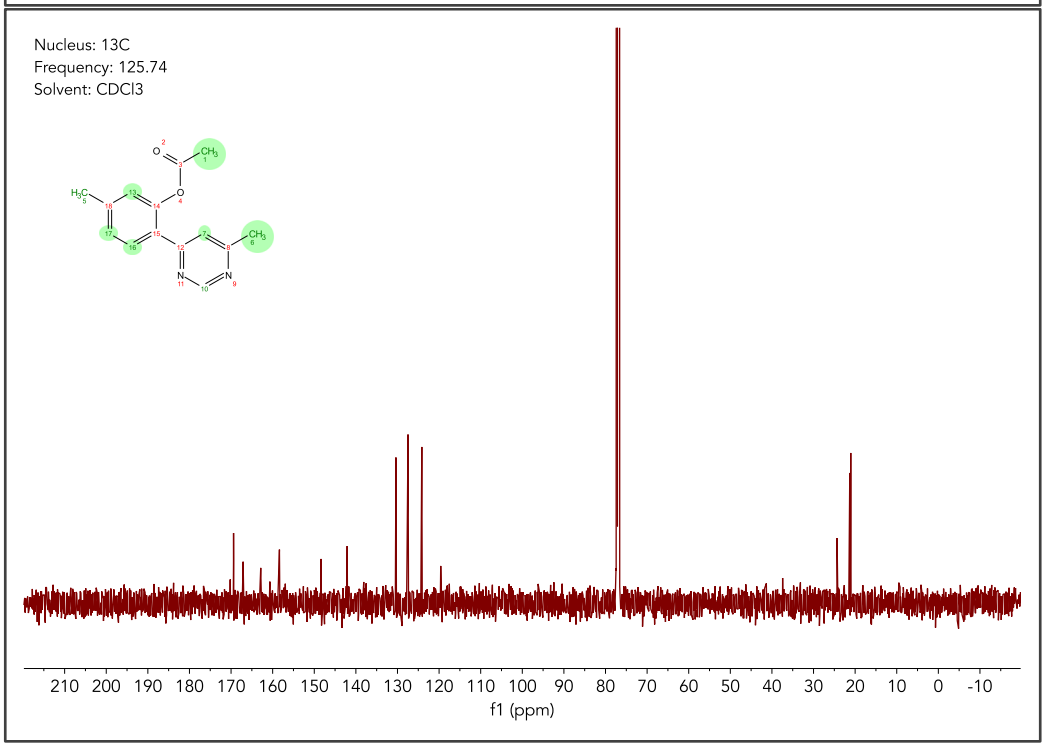

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
12
1.00
0.96
1.07
0.96
1.02
3.24
3.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Nucleus: 13C
Frequency: 150.92
Solvent: CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

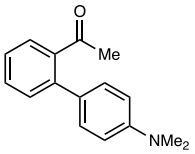
Compound **48**

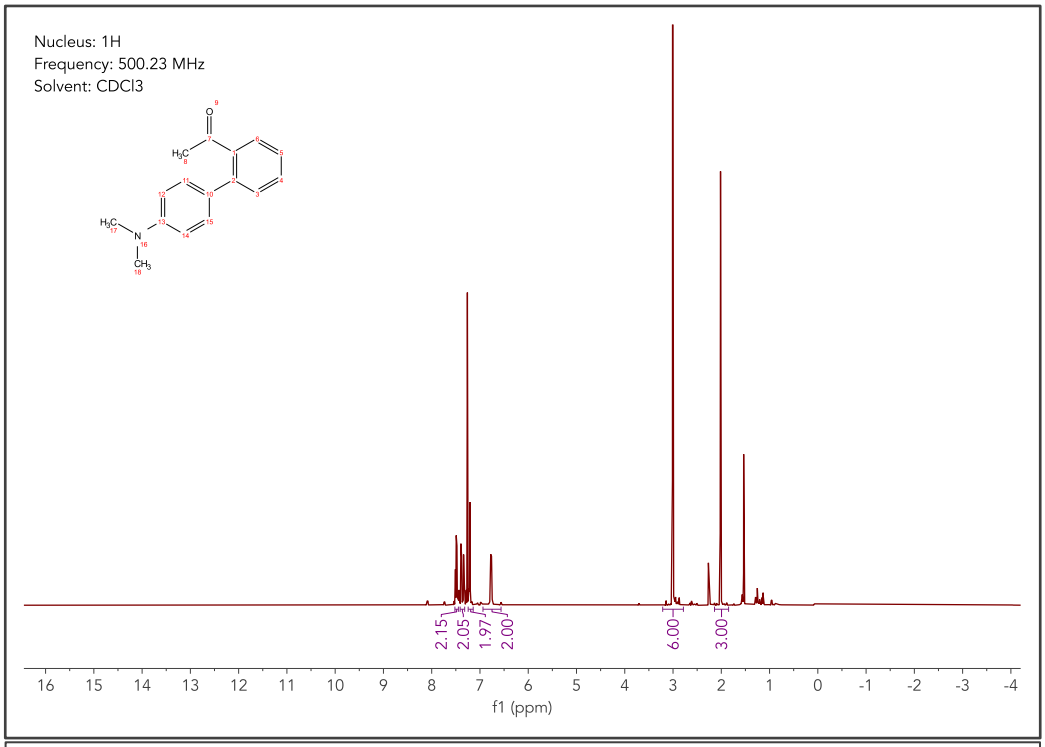

CH3
H3C
N
N
OAc

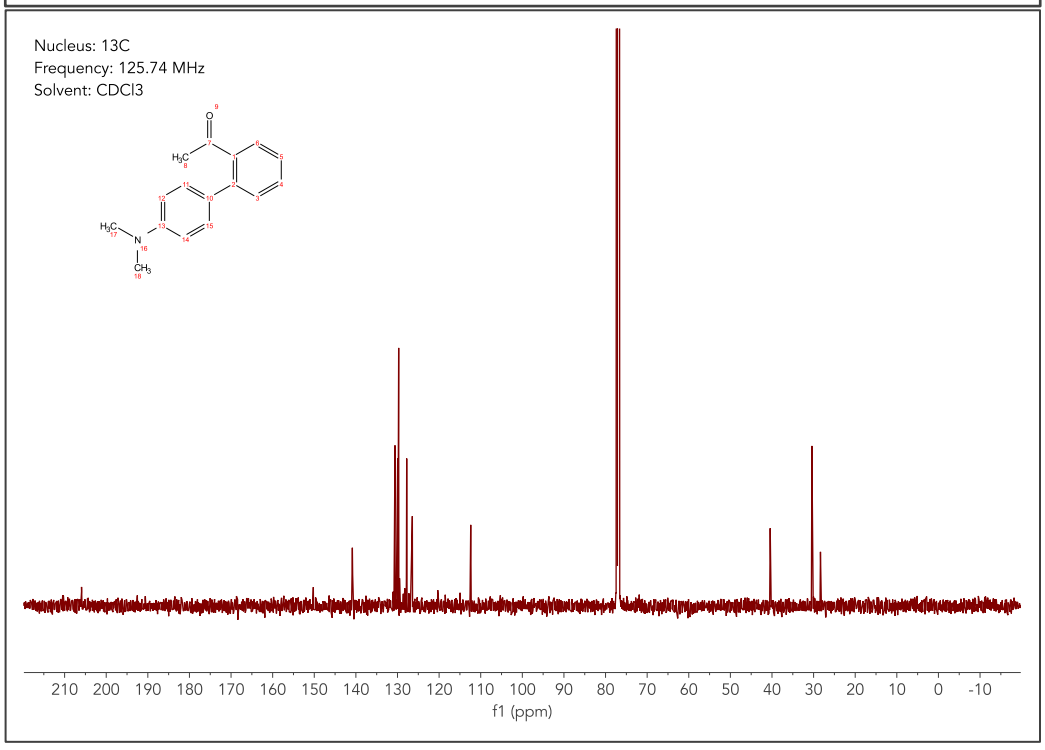

Nucleus: 1H
Frequency: 500.23
Solvent: CDCl3
1.00
1.06
1.01
1.00
1.01
3.08
3.15
3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


Nucleus: 13C
Frequency: 125.74
Solvent: CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

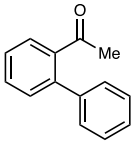
Compound **S49**

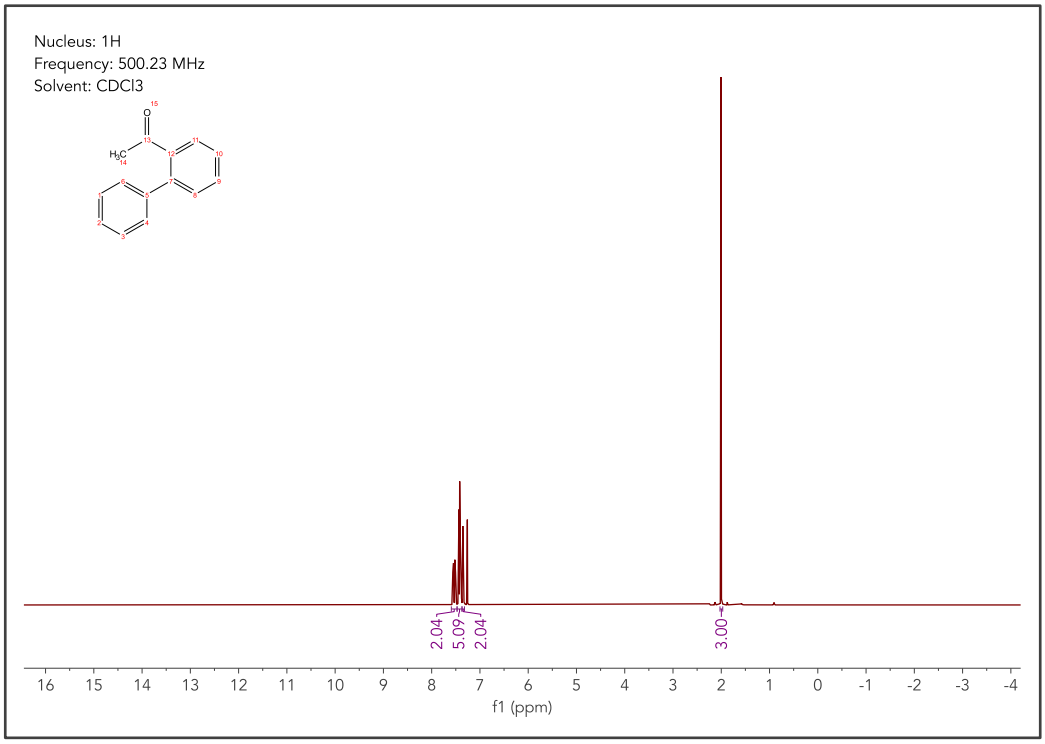




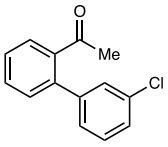


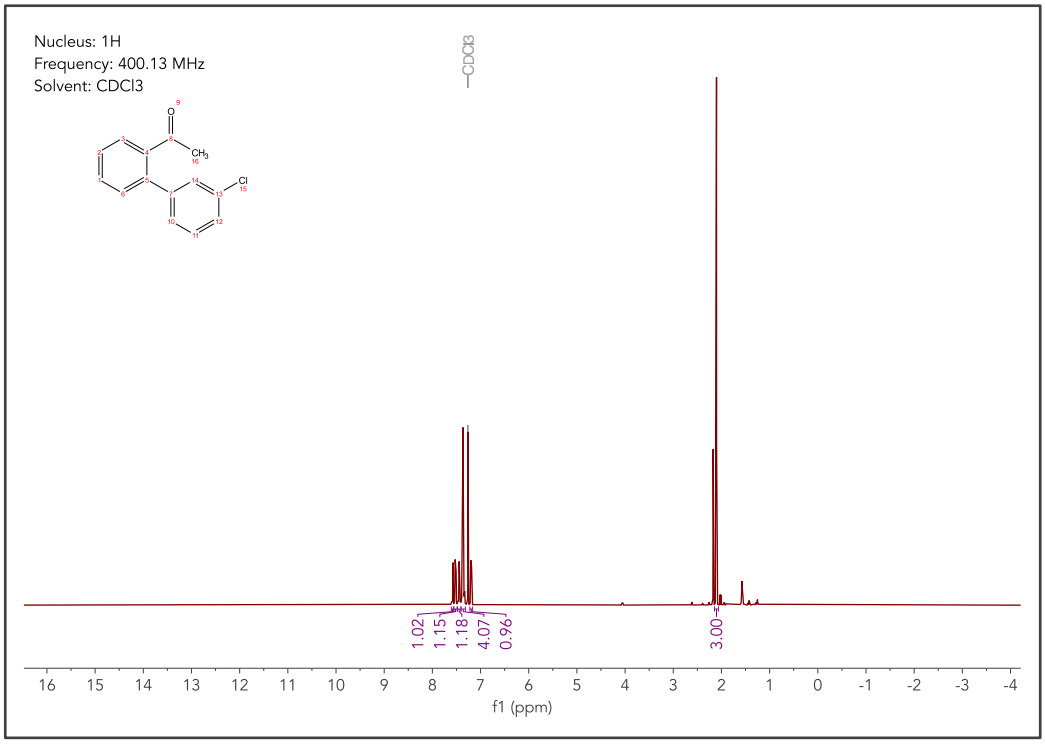
Compound **S50**


O
Me

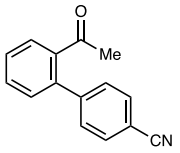

Nucleus: 1H
Frequency: 500.23 MHz
Solvent: CDCl3
2.04
5.09
2.04
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

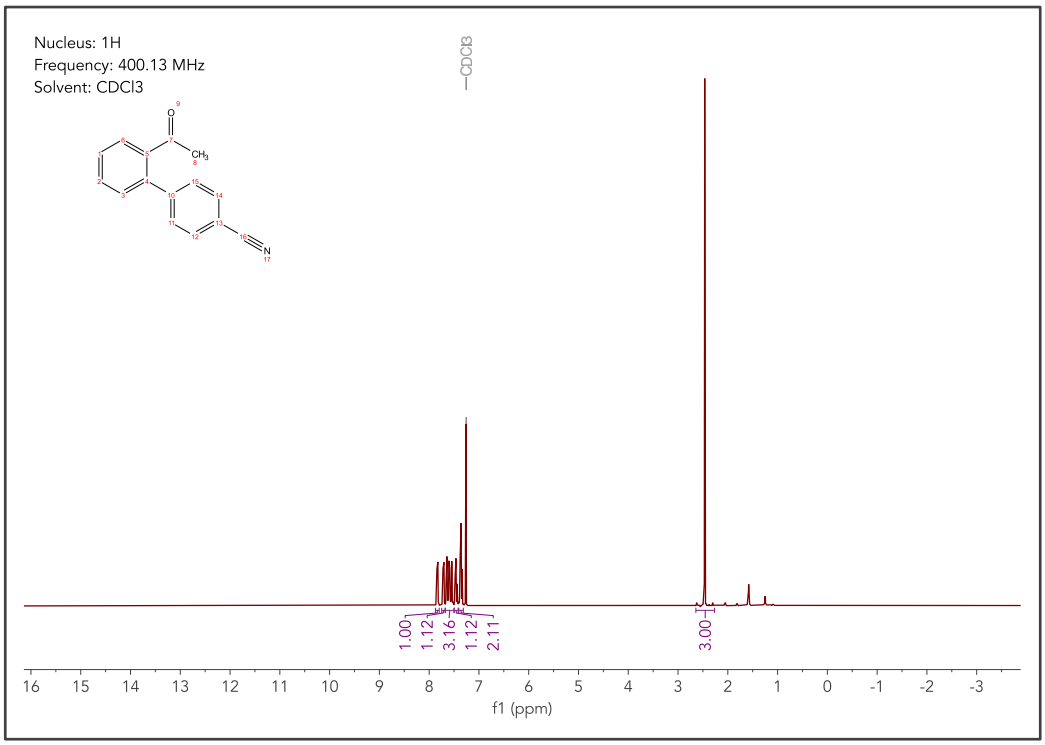
Compound **S51**



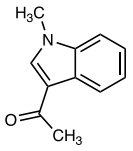


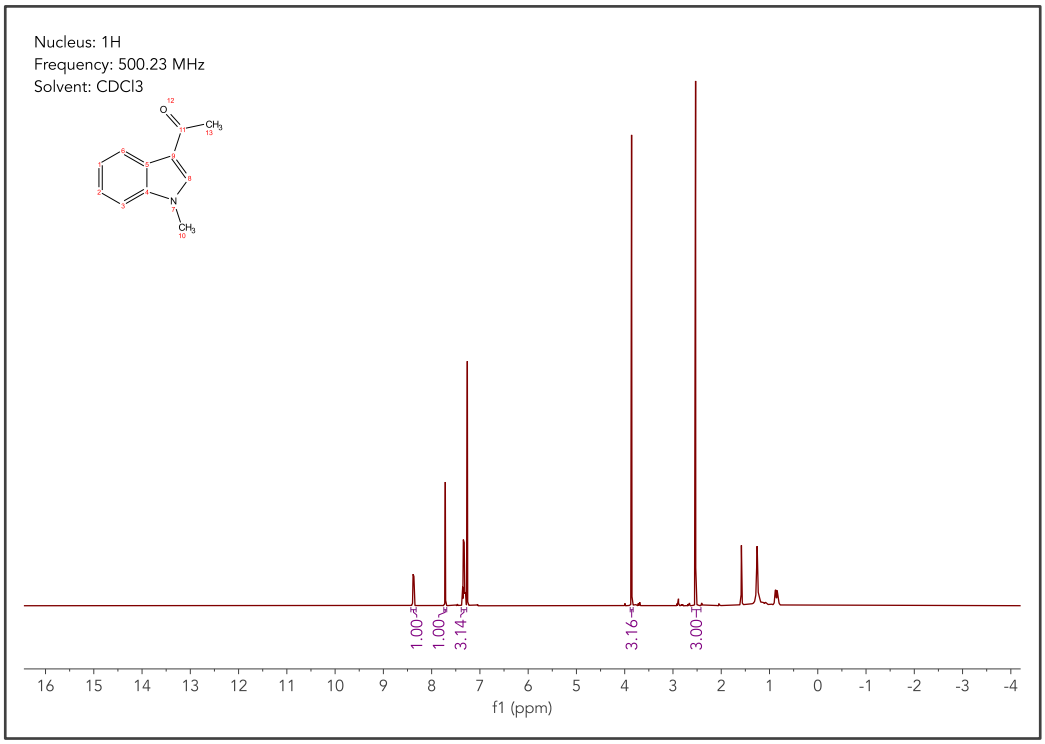
Compound **S52**



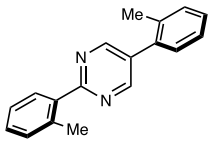


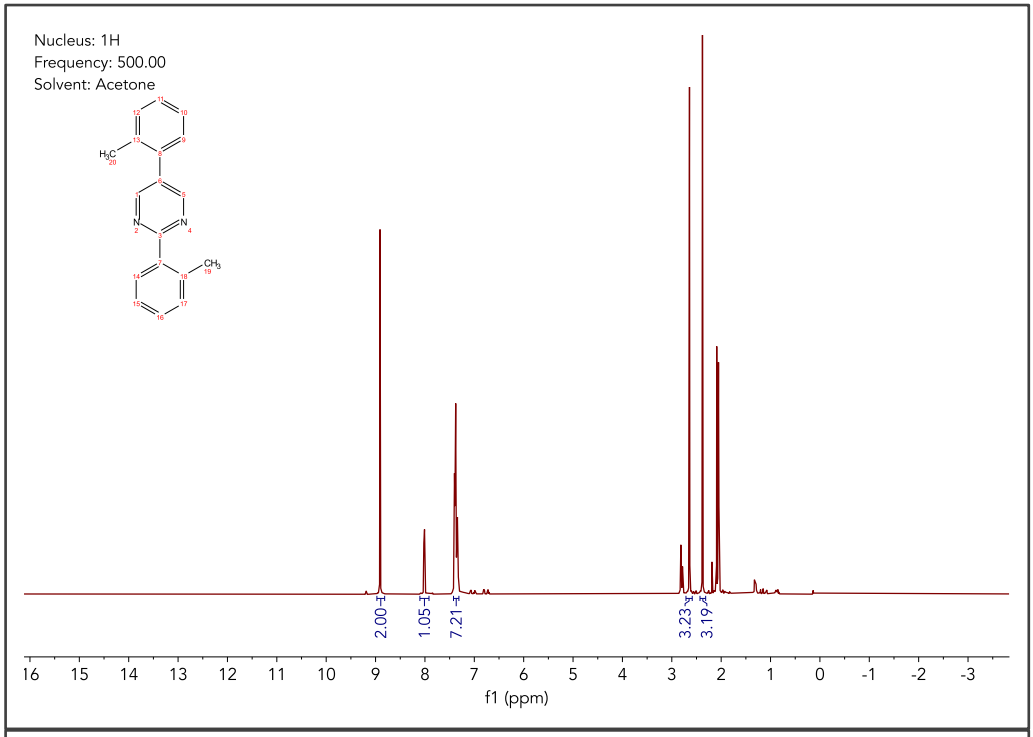
Compound **S53**

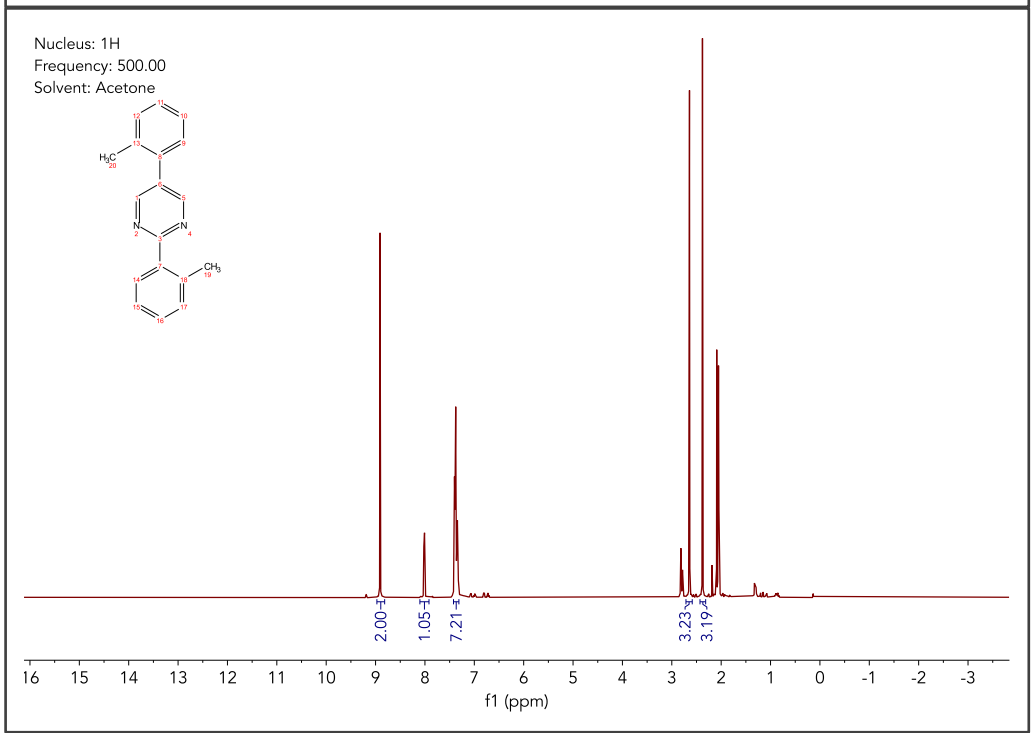




Compound **S54**







6. 2-Aryl Substrates Discussion

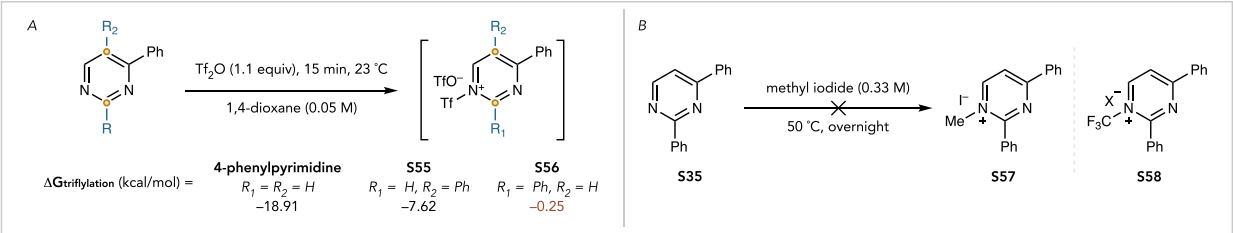


Figure S1. (A) Energetic isothermicity of N-triflylation of 2,4-diphenyl-pyrimidine compared to that of 4-phenylpyrimidine. (B) Intermediacy of a high-energy species in the N-triflylation of 2,4-diphenyl-pyrimidine compared to its isomeric 4,5-diphenylpyrimidine counterpart; methylation of 2,4-diphenylpyrimidine and unsuccessful contraction of the N-methylpyrimidinium intermediate 43, followed by trifluoromethylation of the same substrate to achieve contraction.

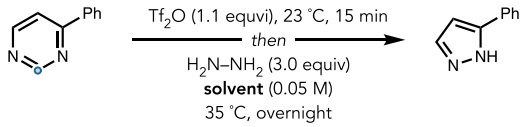
C2-Arylated derivatives **S34–S38**, bearing substituted aryl and heteroaryl linkages, were found to react extremely sluggishly under the typical contraction conditions, giving only trace amounts of the desired contraction products after exposure to the typical conditions over 24 h; accordingly, the yields of the desired contraction products in these cases were extremely low. The diminished reactivity of these 2-aryl substituted substrates likely arises from an unfavorable *N*-triflylation of these substrates, which would lead to a sterically encumbering *N*-triflyl center adjacent to a large phenyl ring. This encumbrance likely leads to rotation of the phenyl ring out of conjugation with the pyrimidine core, further increasing the barrier to *N*-triflylation. To test this hypothesis, 2,5-(*ortho*-toluyl)-pyrimidine, a substrate which is forced to reside in a conformation where the two aryl substituents on the pyrimidine are twisted out of plane, was exposed to the typical contraction conditions by triflylation activation. The dihedral angle between the toluene and pyrimidine rings in this substrate was found to be 11.4° larger than that of the model substrate, 4-phenylpyrimidine, in its ground state conformation. With the energetic penalty of deconjugation accounted for by the conformational ground state destabilization of this substrate, the barrier to triflylation should be lower. Indeed, this substrate was found to contract in 14% yield (^{1}H NMR) under the typical conditions; this low yield likely arises due to incomplete activation indicative of the high energetic penalty imposed by arene deconjugation in the typical 2-aryl substrates. Further investigation into the origin of this effect is ongoing. The energetic costs of C2-arene deconjugation and steric clash are evident in the relative isothermicity of the triflylation of 2,4-diphenyl-pyrimidine, which was calculated to be energetically downhill by only 0.25 kcal/mol as outlined Figure S1A. By comparison, the exothermicity of the triflylation of 4-phenylpyrimidine is over 18 kcal/mol, illustrating the unfavourability of the activation of these 2-aryl substrates. We sought to gain additional insight into this lack of reactivity by comparing the energies of the isomeric intermediates *N*-triflyl-4,5-diphenyl-pyrimidinium (which is free of steric strain upon activation and indeed proceeds to the corresponding pyrazole in 70% yield) with that of *N*-triflyl-2,5-diphenyl-pyrimidine, **S56**, which is unreactive under our optimal conditions Figure S1B. We found $\Delta G°_{triflylation}$ for 4,5-diphenyl-pyrimidine to give **S55** to be more than 7.0 kcal/mol lower than for *N*-triflylation 2,5-diphenyl-pyrimidine to give **S56**, indicating that the relative stability of the triflylated pyrimidinium intermediate significantly impacts the efficiency of this reaction.

To circumvent the challenge of steric encumbrance in the reaction of 2-aryl pyrimidine substrates **S34**–**S38**, we attempted to identify other LUMO-lowering but smaller activating agents. We first returned to methyl iodide, given its documented use as a successful activator for this type of contraction. However, substituting methyl iodide for triflic anhydride in the typical contraction conditions with C2-aryl pyrimidines as substrates led only to the quantitative recovery of starting material. Alternatively, heating the model 2-aryl pyrimidine substrate, 2,4-diphenylpyrimidine (**S35**), at reflux overnight in solvent quantities of methyl iodide failed to yield its *N*-methylated pyrimidinium iodide analogue, **S57**, unfortunately indicating that the previously established *N*-methylation mediated conditions could not be employed for the contraction of these substrates[45,46] This led us to seek out more electrophilic (and more activating), sterically benign activating agents. To this end, *N*-trifluoromethylation was viewed as particularly attractive. Since the LUMO of *N*-trifluoromethylated **S58** was predicted to lie only 3.35 kcal/mol higher than that of its *N*-triflylated counterpart, we investigated the competency of some trifluoromethylating agents to effect the desired contraction by activating the pyrimidine at 40 ˚C for 1 h instead of 35 ˚C for 15 min to facilitate quantitative *N*-trifluoromethylation and then adding the hydrazine at the slightly elevated 40 ˚C as well to account for the raised LUMO of the formed *N*-trifluoromethylpyrimidinium species. Commercially available Togni's reagent and Umemoto's reagent were evaluated for *N*-trifluoromethylation to give **S58**, with initial attempts performed on the model substrate, 4-phenylpyrimidine.

Unfortunately, neither of these trifluoromethylation reagents effected the *N*-trifluoromethylation of 4-phenylpyrimidine, despite the predicted >30 kcal/mol thermodynamic favorability and relatively low calculated barrier of 20 kcal/mol of the reaction. Likely, the lower inherent electrophilicity of the trifluoromethyl donor compared to triflic anhydride is the cause of the observed unreactivity. On this basis, we evaluated the effects of Zn^{II} salts, which are known to activate Togni's reagent by forming dimeric complexes wherein Zn binds 2 to each monomer, thus lengthening the I–O bond and increasing the electrophilicity of the iodine-bound CF_3 unit.[47] Including 50 mol% of $Zn(NTf_2)_2$ with Togni's reagent led to the successful *N*-trifluoromethylation of 4-phenylpyrimidine, permitting the contraction of its activated pyrimidine unit to the desired pyrazole in low (12%) conversion. The conversion of 4-phenlypyrimidine to the desired 5-phenyl-1H-pyrazole increased to 41% at 60 °C. However, increasing the $Zn(NTf_2)_2$ loading from 50 to 100 mol% at 60 ˚C did not increase the conversion, whereas reducing catalyst loading to 10 or 20 mol% at 60 ˚C decreased the conversion to 12% and 19%, respectively. To rule out the possibility that $Zn(NTf_2)_2$ serves as a Lewis acid activator of the pyrimidine core toward hydrazine attack under these conditions, a control reaction was performed in the absence of any electrophilic CF_3 source. In this case, no reactivity was observed, supporting the intermediacy of an *N*-trifluoromethylpyrimidinium species formed by Zn activation of Togni's reagent. A brief solvent screen led to the identification of DME as the optimal solvent for the $Zn(NTf_2)_2$ catalyzed, trifluoromethylation-mediated, contraction of 4-phenylpyrimidine, giving the desired 5-phenyl-1H-pyrazole product in 51% conversion. This may indicate a beneficial effect of ligation of the Zn(II) center, though remains to be fully elucidated. Work to identify conditions for the contraction of these problematic 2-aryl substrates is ongoing.

7. Solvent Screen and Base Screen Data

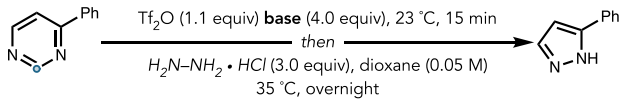
Table S1. Effect of solvent.



entry	solvent	yield (%)[a]
1	**1,4-dioxane**	**90**
2	toluene	64
3	$CHCl_3$	20
4	chlorobenzene	36
5	DME	54
6	THF	75
7	CH_2Cl_2	20
8	DCE	82
9	acetone	0
10	nitromethane	3
11	acetonitrile	80
12	DMF	0

[a]Determined by ^{1}H NMR (ethylene carbonate internal standard, 5.0 mg scale).

Table S2. Effect of base.

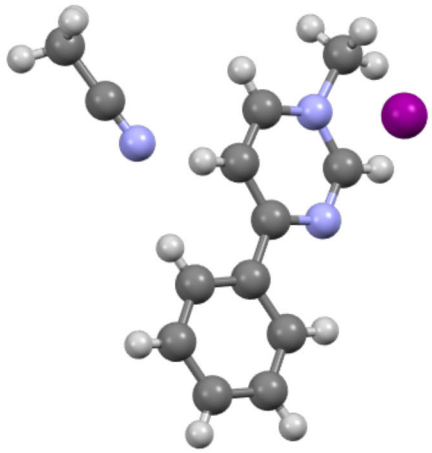


entry	base	yield (%)[a]
1	**Na_2CO_3**	**82**
2	K_2CO_3	48
3	Cs_2CO_3	26
4	K_3PO_4	19
5	DBU	7
6	Et_3N	0
7	pyridine	11
8	DABCO	0

[a]Determined by ^1H NMR (ethylene carbonate internal standard, 5.0 mg scale).

8. X-Ray Crystallographic Information

N-methyl 4-phenyl-pyrimidinium iodide · MeCN



This crystal structure has been deposited at the Cambridge Crystallographic Data Center under CCDC 2210673.

An X-Ray quality crystal was grown by vapor diffusion of hexanes into a nearly saturated solution of *N*-methyl 4-phenyl-pyrimidinium iodide (**1a**) in acetonitrile.

A yellow block 0.21 x 0.14 x 0.09 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame at low and high angles, using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 24965 reflections were collected covering the indices -7<=h<=7, -25<=k<=24, -14<=l<=14. 2880 reflections were founded to be symmetry independent, with an R_{int} of 0.0368. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/c (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.41.122a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Note: The instruments are supported by an NIH Shared Instrument Grant S10-RR027172.

Identification code	LBartholomew02_Sarpong	
Empirical formula	C13 H14 I N3	
Formula weight	339.17	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 5.91980(10) Å	a= 90°.
	b = 20.4062(3) Å	b= 96.2930(10)°.
	c = 11.6838(2) Å	g = 90°.
Volume	1402.91(4) $Å^3$	
Z	4	
Density (calculated)	1.606 Mg/m^3	
Absorption coefficient	17.791 mm^{-1}	
F(000)	664	
Crystal size	0.210 x 0.140 x 0.090 mm^3	
Theta range for data collection	4.333 to 74.470°.	
Index ranges	-7<=h<=7, -25<=k<=24, -14<=l<=14	
Reflections collected	24965	
Independent reflections	2880 [R(int) = 0.0368]	
Completeness to theta = 74.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.29875	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2880 / 0 / 156	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0198, wR2 = 0.0531	
R indices (all data)	R1 = 0.0201, wR2 = 0.0533	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.809 and -0.566 $e.Å^{-3}$	

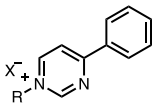
9. Computational Details

9.1 General Workflow

All calculations were performed with Schrödinger Jaguar and MacroModel in Maestro. Conformation searches by mixed torsional and low-mode sampling using the OPLS4[48] force field in chloroform were performed for all molecules and intermediates exhaustively prior to DFT employment using MacroModel. Ground state and transition state geometries were optimized first using the range-separated ωB97X-D[49] density functional with empirical dispersion correction and the 6-31G(d,p)[50] basis set in the gas phase. Ground state energies were then refined by single point energy calculations using the wB97X density functional with Grimme's D3 empirical dispersion correction[51,52] and Becke-Johnson damping[53] and the triple zeta def2-TZVP[54] basis set. The polarizable continuum model (PCM) was employed for solvation corrections (THF). Initial transition state guesses (ωB97X-D[49] / 6-31G(d,p)[50], PCM (THF)) were refined by the quadratic synchronous transit (QST) method with the with the ωB97X-D3(BJ)[49] density functional and the def2-TZVP[54] basis set under an ultrafine convergence threshold and a fine grid density using quantum mechanical initial Hessian guesses (to match final ground state calculation parameters). Once reasonable transition states with single imaginary frequencies were obtained, intrinsic reaction coordinate scans were performed on each identified transition state structure to verify that the identified transition state lied on the path between the corresponding starting materials and products. 3D images of the structures of molecules and intermediates were generated using CYLview20.

9.2 LUMO energies of various activated pyrimidines

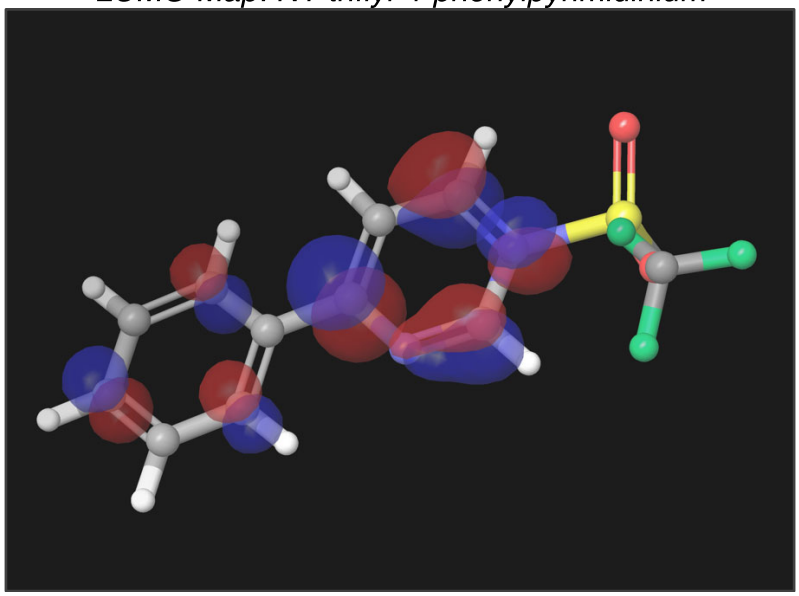
Table S2. LUMOs of activated pyrimidines.



Entry	R	X⁻	LUMO (eV)[a]
1	$Ti(OiPr)_3$	iPrO⁻	–2.30
2	Me	I⁻	–3.13
3	H	TFAO⁻	–3.16
4	PhOCO	Cl⁻	–3.81
5	CF_3	I⁻	–3.73
6	CF_2H	Cl⁻	–3.48
7	BF_3	–	–2.87
8	BCl_3	–	–3.08
9	BBr_3	–	–3.14
10	TMS	TfO⁻	–3.12
11	allyl	Br⁻	–2.52
12	**Tf**	**TfO⁻**	**–3.88**

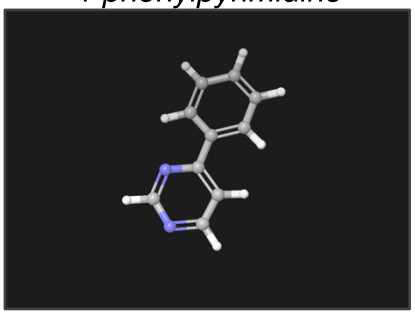
[a]wB97x-D3(BJ), def2-TZVP(-f), dioxane (SM8).

LUMO Map: N1-triflyl-4-phenylpyrimidinium

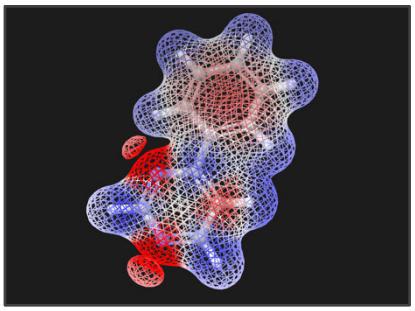


9.3 Computed electronic surfaces of 4-phenylpyrimidine (S1)

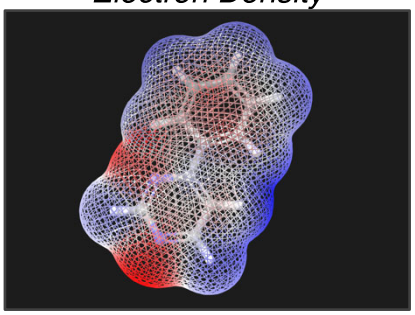
4-phenylpyrimidine



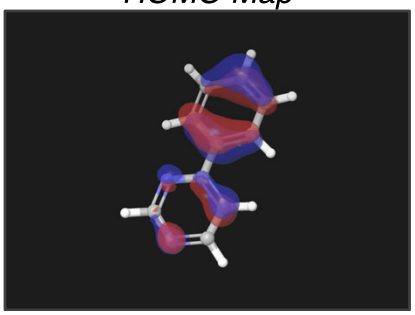
Electrostatic Potential



Electron Density



HOMO Map



Energetics for N-triflylation of 4-phenylpyrimidine (A, S1)

The calculated energy of **A** + Tf_2O varied widely using different solvation models. The most reasonable calculated ground state energy of the system at this stage (**A** + Tf_2O + 2 equiv hydrazine) lies 67.27 kcal/mol above the final products (**I** + triflylformamidine + hydrazinium triflate). However, the calculated barriers for triflylation remain within 0.1 kcal/mol regardless of solvation model: specifically, $\Delta G^{\ddagger}_{triflylation} \approx 1.0$ kcal/mol, as shown in Figure S2.

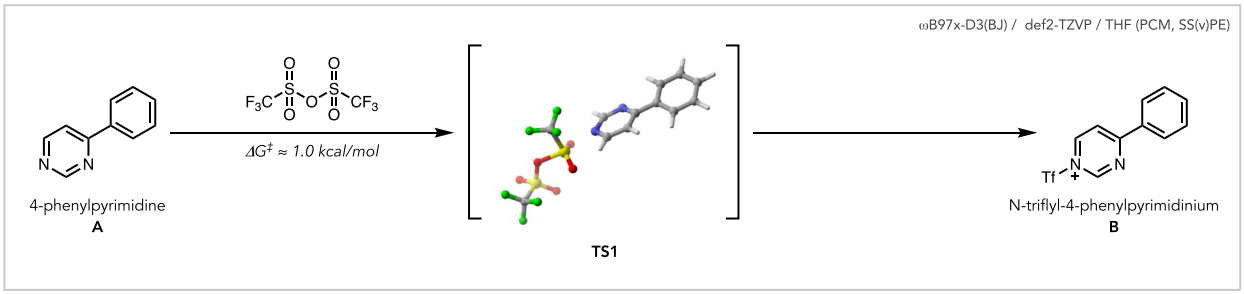
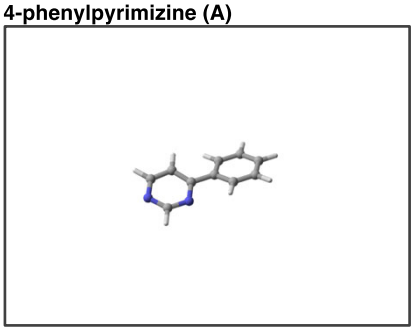


Figure S2. Low-barrier N-triflylation of **A** with triflic anhydride to give **B.**

9.4 Cartesian coordinates (Å) and Energies (Hartrees) of Optimized Structures

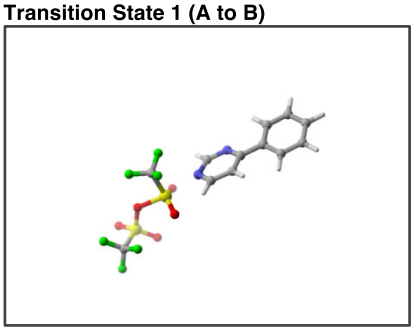
4-phenylpyrimizine (A)



Solution phase energy (Hartrees) = -495.780004

C	4.56190	-1.90770	2.51290
N	3.72590	-0.85770	2.57160
C	2.46770	-1.11410	2.19320
N	1.97170	-2.27430	1.76050
C	2.82060	-3.32300	1.69540
C	4.15950	-3.16730	2.08720
C	2.27190	-4.61550	1.21760
C	0.88780	-4.85290	1.27570
C	0.35760	-6.06560	0.84110
C	1.19980	-7.05820	0.33270
C	2.57600	-6.82900	0.26060
C	3.10940	-5.61860	0.70030
H	5.58890	-1.73280	2.82590
H	1.76870	-0.28090	2.24040
H	4.85930	-3.99350	2.08140
H	0.23730	-4.08060	1.67050
H	-0.71300	-6.23720	0.90020
H	0.78620	-8.00260	-0.00830
H	3.23500	-7.59110	-0.14400
H	4.17830	-5.45130	0.61650

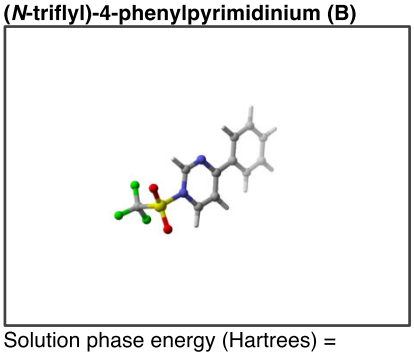
Transition State 1 (A to B)



Solution phase energy (Hartrees) = -2344.049471

C	1.56510	-1.44780	-2.44210
N	0.62530	-1.60780	-1.50540
C	-0.48020	-2.26590	-1.84580
N	-0.72120	-2.79320	-3.03290
C	0.21320	-2.65310	-3.98820
C	1.40020	-1.95790	-3.71930
C	-0.08640	-3.26170	-5.30640
C	0.92890	-3.52600	-6.23540
C	0.62130	-4.10900	-7.46300
C	-0.70040	-4.43090	-7.77630
C	-1.71560	-4.17510	-6.85250
C	-1.41000	-3.59960	-5.62290
S	1.02650	-1.24130	0.86790
O	2.41440	-1.37710	0.52550
O	0.04520	-2.26960	1.06800
O	1.16950	-0.61120	2.60140
C	0.27180	0.43150	0.33940
F	-0.89760	0.18810	-0.20120
F	0.12140	1.22700	1.36890
F	1.10530	0.96430	-0.52270
S	1.84010	-1.50260	3.71830
O	1.04410	-1.41740	4.91920
O	2.26640	-2.77550	3.18160
C	3.35390	-0.47910	3.98890
F	3.98910	-0.32550	2.84030
F	3.00830	0.70250	4.47030
F	4.13860	-1.09950	4.85340
H	2.46910	-0.91010	-2.16140
H	-1.24080	-2.39090	-1.07870
H	2.16680	-1.79790	-4.46920
H	1.96600	-3.29790	-6.00480
H	1.41540	-4.31530	-8.17540
H	-0.93820	-4.88260	-8.73590
H	-2.74610	-4.42690	-7.08960
H	-2.19620	-3.40030	-4.90210

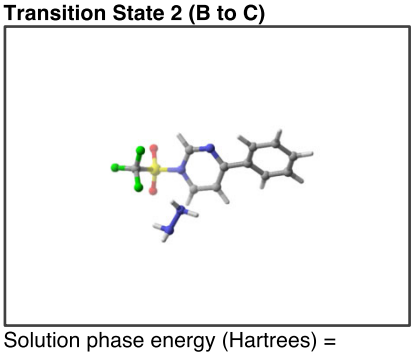
(*N*-triflyl)-4-phenylpyrimidinium (B)



Solution phase energy (Hartrees) = -1382.104003

C	1.26240	-5.14090	3.86190
N	0.60730	-4.06410	4.38950
C	0.34350	-2.97140	3.60980
N	0.66350	-2.91520	2.35010
C	1.28980	-3.97420	1.76170
C	1.61800	-5.11300	2.54140
C	1.59450	-3.85780	0.34240
C	2.10280	-4.95070	-0.39370
C	2.38230	-4.81230	-1.74710
C	2.16680	-3.58720	-2.38720
C	1.66340	-2.49700	-1.66970
C	1.37460	-2.62810	-0.31790
S	0.09410	-4.08350	6.11890
O	0.95760	-5.04840	6.77160
O	-0.03680	-2.69170	6.50330
C	-1.63270	-4.84420	5.85720
F	-1.46350	-6.03620	5.30730
F	-2.21750	-4.93760	7.03510
F	-2.30480	-4.04140	5.04730
H	1.47640	-5.96760	4.52770
H	-0.15130	-2.13440	4.09020
H	2.14950	-5.96110	2.13420
H	2.26650	-5.91270	0.07680
H	2.76630	-5.65860	-2.30620
H	2.38970	-3.48370	-3.44460
H	1.49750	-1.54720	-2.16660
H	0.98540	-1.78740	0.24290

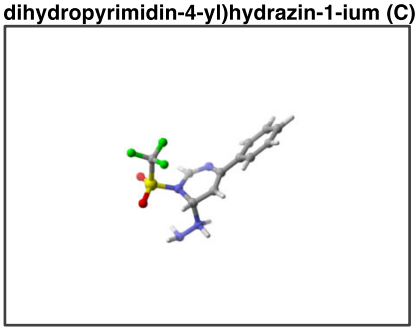
Transition State 2 (B to C)



Solution phase energy (Hartrees) = -1494.033676

C	1.25760	-3.26990	3.46480
N	0.36610	-4.20450	3.93060
C	-0.25540	-5.08500	3.06760
N	0.01060	-5.10660	1.80890
C	0.99890	-4.29560	1.31700
C	1.65200	-3.38580	2.13510
C	1.30970	-4.44900	-0.10900
C	0.29810	-4.85900	-0.99130
C	0.56690	-4.96910	-2.35150
C	1.85110	-4.70410	-2.83290
C	2.86650	-4.32040	-1.95320
C	2.59780	-4.18040	-0.59540
N	0.00390	-1.28660	3.30850
N	0.45880	-0.32220	4.27080
S	0.10250	-4.37750	5.64750
O	-0.02880	-5.78550	5.89370
O	1.03700	-3.49010	6.28210
C	-1.59720	-3.62660	5.80430
F	-1.54370	-2.36110	5.43870
F	-2.42750	-4.29230	5.02460
F	-1.96230	-3.72850	7.06090
H	1.82100	-2.69720	4.19490
H	-0.97890	-5.78270	3.48930
H	2.42180	-2.71530	1.76670
H	-0.69660	-5.07060	-0.60960
H	-0.22350	-5.26310	-3.03710
H	2.06220	-4.80200	-3.89460
H	3.87000	-4.13490	-2.32540
H	3.39920	-3.90220	0.08520
H	-1.01830	-1.31870	3.24870
H	0.32460	-0.97430	2.39080
H	0.25580	-0.68570	5.20080
H	-0.06970	0.55130	4.18930

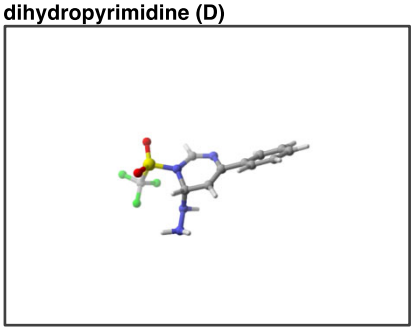
1-(6-phenyl-3-((trifluoromethyl)sulfonyl)-3,4-dihydropyrimidin-4-yl)hydrazin-1-ium (C)



Solution phase energy (hartrees) = -1494.089554

C	2.84720	0.61610	2.94940
N	2.45380	-0.77670	2.80900
C	2.07910	-1.23900	1.51640
N	1.69110	-0.44620	0.60230
C	1.50120	0.91990	0.91640
C	2.07660	1.47540	2.00430
C	0.61210	1.64670	-0.02500
C	0.04730	2.88320	0.32640
C	-0.78680	3.55440	-0.56400
C	-1.07860	2.99820	-1.81300
C	-0.53510	1.76180	-2.16220
C	0.30330	1.08760	-1.27380
N	4.37370	0.72930	2.69180
N	5.20560	-0.11820	3.48970
S	1.97370	-1.69630	4.12950
O	2.08990	-3.08720	3.76060
O	2.57550	-1.12230	5.31010
C	0.14210	-1.33580	4.20860
F	-0.40510	-1.67850	3.05190
F	-0.39140	-2.03660	5.18970
F	-0.02930	-0.04120	4.41970
H	2.73610	0.94150	3.98940
H	2.14620	-2.31550	1.35880
H	1.98500	2.52690	2.25730
H	0.23450	3.32150	1.30320
H	-1.21870	4.50960	-0.27820
H	-1.73230	3.52320	-2.50480
H	-0.76400	1.31720	-3.12730
H	0.72010	0.12470	-1.54830
H	4.61430	0.57400	1.69380
H	4.64800	1.71280	2.87630
H	4.96930	0.02570	4.47720
H	5.03600	-1.09380	3.22840

6-hydrazineyl-4-phenyl-1-((trifluoromethyl)sulfonyl)-1,6-dihydropyrimidine (D)

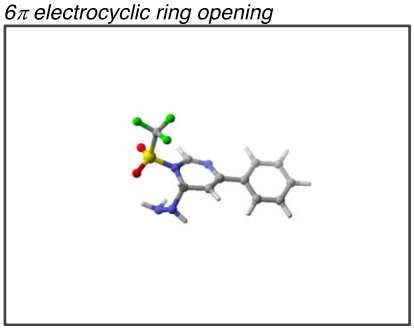


Solution phase energy (Hartrees) = -1493.645224

C	3.05630	0.92580	3.32160
N	4.05150	0.35050	2.39790
C	4.41930	1.07460	1.25910
N	3.67150	1.95030	0.71410
C	2.38270	2.11920	1.25700
C	2.05420	1.64890	2.47120
C	1.43370	2.82700	0.36840
C	0.07030	2.52550	0.38990
C	-0.80830	3.18000	-0.46240
C	-0.33450	4.14270	-1.34660
C	1.02310	4.44270	-1.37810
C	1.90460	3.78380	-0.53270
N	3.73960	1.74550	4.31890
N	3.11470	1.85870	5.58310
S	4.93920	-0.98200	2.87190
O	4.08110	-1.82790	3.67010
O	5.66950	-1.44110	1.71170
C	6.23410	-0.29230	4.03280
F	5.75150	-0.16600	5.25580
F	7.24760	-1.14650	4.05090
F	6.65430	0.88040	3.57910
H	2.59280	0.09450	3.85860
H	5.39330	0.83620	0.84300
H	1.07480	1.83150	2.89840
H	-0.29850	1.74480	1.04750
H	-1.86250	2.92300	-0.44960
H	-1.02000	4.64750	-2.01960
H	1.39920	5.18810	-2.07140
H	2.96740	3.99590	-0.56630
H	3.89790	2.68220	3.96250
H	3.36830	1.04390	6.13070
H	2.09950	1.89830	5.50980

Transition State 3 (D to E)

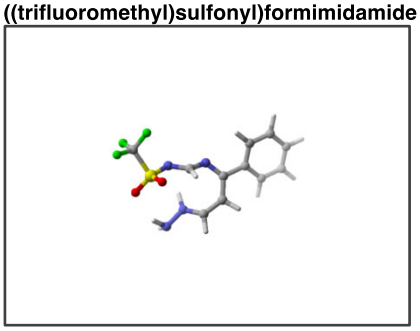
6π electrocyclic ring opening



Solution phase energy (Hartrees) = -1493.634365

C	1.63920	2.19700	3.44190
N	1.24540	0.80910	3.46360
C	0.93470	0.11900	2.28320
N	0.70650	0.68380	1.16670
C	0.70850	2.09730	1.13230
C	1.08420	2.82380	2.19480
C	0.22320	2.69170	-0.13740
C	0.61810	3.97450	-0.53620
C	0.12960	4.53050	-1.71330
C	-0.75520	3.81120	-2.51410
C	-1.14240	2.52900	-2.13260
C	-0.65370	1.97100	-0.95570
N	3.12270	2.41030	3.55680
N	3.98410	1.29380	3.44490
S	1.29400	-0.04530	4.90040
O	1.55130	-1.43960	4.61030
O	2.07850	0.70950	5.85280
C	-0.47860	0.06770	5.45850
F	-1.25390	-0.48540	4.53890
F	-0.60370	-0.57580	6.60580
F	-0.80230	1.34220	5.61380
H	1.19200	2.68030	4.31410
H	0.89950	-0.96160	2.37890
H	1.03250	3.90610	2.19150
H	1.32850	4.53550	0.06300
H	0.44930	5.52390	-2.01100
H	-1.13420	4.24500	-3.43390
H	-1.82780	1.96020	-2.75270
H	-0.95340	0.97140	-0.66100
H	3.38520	3.05090	2.81380
H	4.01560	0.81800	4.33910
H	3.69290	0.62650	2.73260

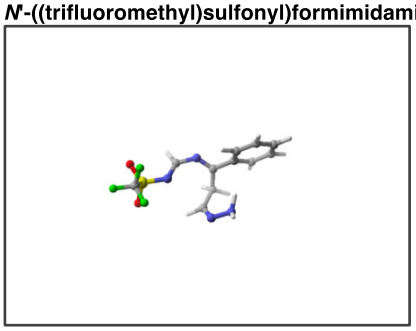
(*E*)-*N*-((1*E*,2*E*)-3-hydrazineyl-1-phenylallylidene)-*N'*-((trifluoromethyl)sulfonyl)formimidamide (E)



Solution phase energy (Hartrees) = -1493.641965

C	-0.48820	0.81410	1.97570
N	-3.50360	1.84590	3.66930
C	-3.35590	1.21100	2.52990
N	-3.33120	-0.11690	2.45370
C	-2.48960	-0.68030	1.60140
C	-1.24780	-0.08300	1.24000
C	-2.87180	-1.97330	0.98520
C	-4.22450	-2.29770	0.84020
C	-4.59830	-3.47330	0.20350
C	-3.62620	-4.34240	-0.28510
C	-2.27770	-4.03750	-0.12780
C	-1.90190	-2.85970	0.50430
N	-0.60560	1.19900	3.24210
N	0.24790	2.20330	3.73190
S	-3.39880	3.48090	3.56130
O	-2.32180	3.93440	4.43590
O	-3.47670	4.01010	2.20320
C	-4.98530	3.95620	4.38970
F	-6.00680	3.46110	3.70120
F	-5.01680	3.48630	5.62880
F	-5.07360	5.28050	4.41650
H	0.38480	1.25130	1.49930
H	-3.23070	1.77420	1.59470
H	-0.79420	-0.39620	0.30720
H	-4.97540	-1.61080	1.21640
H	-5.64970	-3.71090	0.08100
H	-3.91960	-5.25890	-0.78710
H	-1.51770	-4.71830	-0.49640
H	-0.84910	-2.63510	0.64010
H	-1.37620	0.89130	3.82480
H	0.67630	1.85800	4.58610
H	-0.33660	3.00200	3.98230

(*E*)-*N*-((1*E*,3*E*)-3-hydrazineylidene-1-phenylpropylidene)-*N'*-((trifluoromethyl)sulfonyl)formimidamide (F)

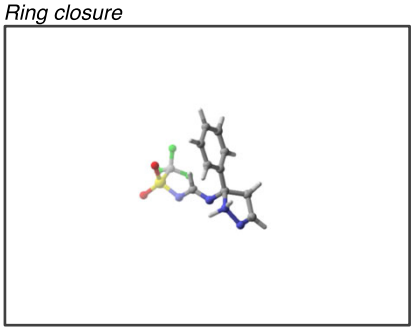


Solution phase energy (Hartrees) = -1493.631608

C	4.17800	-1.59620	-2.85960
N	4.54980	0.61520	-4.84420
C	3.54610	0.21450	-5.56220
N	3.46240	-1.08320	-5.93570
C	3.28930	-2.11920	-5.20440
C	2.99280	-2.03860	-3.71130
C	3.39210	-3.45380	-5.85250
C	4.40000	-3.68810	-6.79990
C	4.51680	-4.94370	-7.39290
C	3.60830	-5.95620	-7.07220
C	2.58960	-5.71780	-6.14670
C	2.49130	-4.47580	-5.52110
N	5.24520	-2.24940	-2.61190
N	5.41410	-3.51580	-3.13490
S	4.69610	2.22300	-4.55800
O	3.98440	3.08000	-5.50090
O	4.58400	2.48580	-3.13020
C	6.50180	2.39150	-4.95640
F	6.73080	2.00270	-6.20370
F	6.83800	3.67010	-4.82510
F	7.22540	1.65960	-4.12290
H	4.09750	-0.62920	-2.37050
H	2.78670	0.88610	-5.98030
H	2.17710	-1.32390	-3.56000
H	5.10230	-2.89510	-7.04810
H	5.31570	-5.13220	-8.10500
H	3.69360	-6.93200	-7.54370
H	1.87320	-6.49950	-5.90910
H	1.69190	-4.29530	-4.80590
H	2.65200	-3.01550	-3.35030
H	4.99650	-3.67430	-4.05040
H	6.40550	-3.74800	-3.16090

Transition State 4 (F to G)

Ring closure

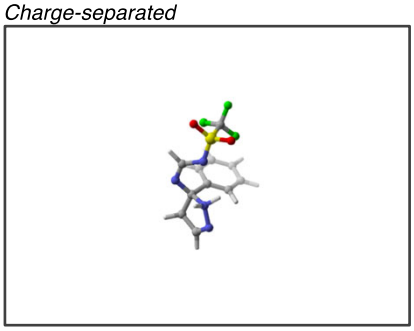


Solution phase energy (Hartrees) = -1493.614557

C	3.01630	-2.33820	-1.07390
N	5.86110	0.36910	-4.43780
C	5.06640	-0.73370	-4.42410
N	4.57290	-1.16390	-3.31370
C	3.73380	-2.36340	-3.31630
C	2.49710	-2.07910	-2.44770
C	3.44400	-2.99150	-4.65860
C	2.48780	-2.36700	-5.47140
C	2.30660	-2.77830	-6.78920
C	3.11970	-3.77810	-7.32740
C	4.08800	-4.38530	-6.53100
C	4.26840	-3.97450	-5.20880
N	4.08260	-3.03230	-1.00020
N	4.48200	-3.35830	-2.36020
S	6.33500	0.89510	-5.86050
O	7.53770	1.71290	-5.70100
O	6.32000	-0.10260	-6.93670
C	5.01960	2.13070	-6.40150
F	4.13400	2.33640	-5.43180
F	5.57390	3.29390	-6.72070
F	4.36520	1.67090	-7.46360
H	2.54050	-1.99540	-0.15630
H	4.88380	-1.24260	-5.37870
H	2.13000	-1.05670	-2.57240
H	1.84580	-1.58570	-5.06690
H	1.54200	-2.30640	-7.40090
H	2.99120	-4.08800	-8.36110
H	4.72380	-5.16480	-6.94170
H	5.04100	-4.45710	-4.61220
H	1.66950	-2.77160	-2.65260
H	4.24110	-4.35400	-2.51490
H	5.51130	-3.28410	-2.42510

Ring-closed intermediate (G)

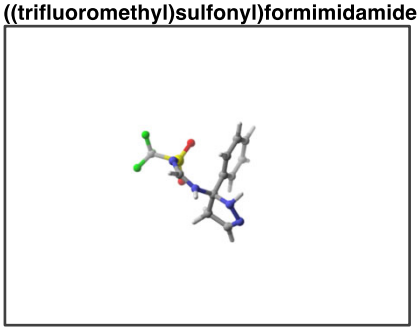
Charge-separated



Solution phase energy (Hartrees) =
-1493.651585

C	2.46170	-5.03130	0.78280
N	3.34510	-0.78080	2.71430
C	1.99220	-0.91450	2.67450
N	1.39630	-1.87500	2.03650
C	2.24440	-2.71380	1.22510
C	1.46910	-3.92230	0.65740
C	2.94940	-1.96330	0.08060
C	4.21360	-2.31230	-0.40710
C	4.75220	-1.64640	-1.51330
C	4.03370	-0.63570	-2.15070
C	2.76820	-0.29120	-1.67350
C	2.23000	-0.95120	-0.56990
N	3.45730	-4.81390	1.55400
N	3.29010	-3.47330	2.09590
S	3.95820	0.57400	3.26160
O	3.06910	1.38510	4.10530
O	5.33030	0.36050	3.72380
C	4.14670	1.59000	1.71850
F	4.70620	2.76510	2.01040
F	4.90670	0.96170	0.82950
F	2.94650	1.81060	1.18310
H	2.38550	-5.99570	0.28210
H	1.35660	-0.21000	3.21980
H	0.58600	-4.14880	1.26980
H	4.80770	-3.10210	0.05070
H	5.73780	-1.92560	-1.87780
H	4.45390	-0.12180	-3.01220
H	2.19400	0.49330	-2.16090
H	1.24190	-0.67250	-0.21390
H	1.14550	-3.76550	-0.37490
H	4.20400	-2.99970	2.15450
H	2.96640	-3.56840	3.07790

(*R*,*E*)-*N*-(5-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-*N*'-((trifluoromethyl)sulfonyl)formimidamide (H)

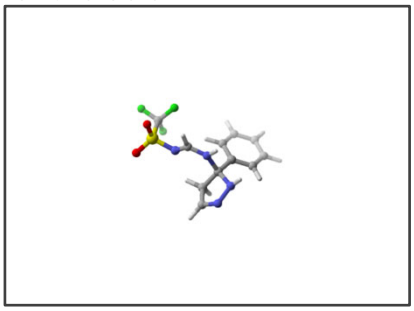


Solution phase energy (Hartrees) =
-1493.661641

C	2.77910	1.33920	0.73200
N	5.68110	-2.47910	3.20280
C	4.44260	-2.12680	3.47890
N	3.52640	-1.40740	2.84730
C	3.46540	-0.76910	1.51640
C	3.88360	0.72120	1.54020
C	4.10510	-1.62690	0.42490
C	4.77030	-1.04460	-0.65980
C	5.22920	-1.83740	-1.71250
C	5.02940	-3.21740	-1.69440
C	4.35720	-3.80330	-0.62050
C	3.89260	-3.01190	0.42820
N	1.77700	0.56260	0.56100
N	2.00830	-0.63740	1.24020
S	6.73270	-1.86180	2.15470
O	6.58100	-0.43150	1.89260
O	7.04570	-2.76470	1.05490
C	8.23500	-1.95430	3.23040
F	8.08180	-1.22480	4.33020
F	8.50130	-3.21010	3.57120
F	9.26540	-1.47170	2.53620
H	2.76990	2.35510	0.34540
H	4.06940	-2.54150	4.41780
H	3.86200	1.10300	2.56880
H	4.94910	0.02590	-0.69970
H	5.74650	-1.37030	-2.54730
H	5.39220	-3.83270	-2.51430
H	4.19280	-4.87790	-0.59780
H	3.36020	-3.48100	1.25360
H	4.87890	0.90870	1.14430
H	1.61480	-1.42120	0.71890
H	2.64930	-1.31120	3.36190

Transition State 5 (H to I)

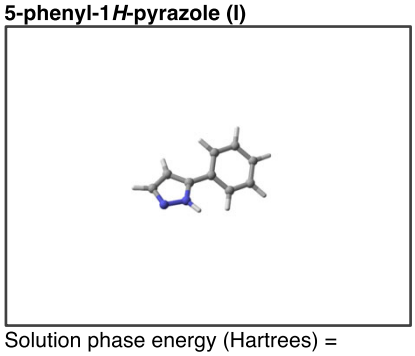
Formal retro ene



Solution phase energy (Hartrees) = -1493.652807

C	3.22080	-2.59540	-1.53720
N	4.43110	0.13960	-3.92350
C	5.48850	-0.62680	-3.73320
N	5.40430	-1.93560	-3.62800
C	4.20000	-2.83550	-3.64920
C	2.97880	-2.18570	-2.95990
C	3.91200	-3.30250	-5.06880
C	3.65640	-4.64710	-5.33940
C	3.32490	-5.05550	-6.63280
C	3.23440	-4.12050	-7.66210
C	3.47980	-2.77220	-7.39350
C	3.81680	-2.36630	-6.10390
N	4.05850	-3.55610	-1.44150
N	4.45920	-3.92540	-2.72500
S	4.64640	1.72430	-4.06850
O	3.59310	2.44300	-3.36340
O	6.03010	2.17590	-3.92700
C	4.23660	1.93330	-5.85910
F	2.99050	1.54990	-6.09880
F	4.37010	3.20770	-6.20040
F	5.06240	1.19840	-6.59830
H	2.71330	-2.19480	-0.66540
H	6.50120	-0.22040	-3.65090
H	2.91140	-1.11520	-3.12940
H	3.70740	-5.37130	-4.53360
H	3.13310	-6.10720	-6.82990
H	2.97350	-4.43800	-8.66840
H	3.40400	-2.03640	-8.19030
H	3.98690	-1.31340	-5.89990
H	6.30010	-2.41440	-3.51560
H	2.06370	-2.66380	-3.33150
H	5.37810	-4.36540	-2.73980

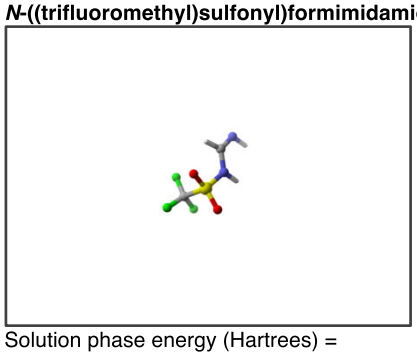
5-phenyl-1*H*-pyrazole (I)



Solution phase energy (Hartrees) = -457.634006

C	2.37870	-0.81640	-3.90440
C	3.47560	-0.04010	-2.13390
C	3.14690	-1.22030	-2.79500
C	4.24990	0.20330	-0.91260
C	4.03130	1.34650	-0.12340
C	4.78040	1.56210	1.03310
C	5.75130	0.63760	1.42620
C	5.97030	-0.50570	0.65240
C	5.23020	-0.72030	-0.50900
N	2.22980	0.51200	-3.95290
N	2.89880	0.95650	-2.86570
H	1.92400	-1.43550	-4.66660
H	3.25590	2.05650	-0.39620
H	4.59630	2.44800	1.63350
H	6.33100	0.80530	2.32890
H	6.72570	-1.22740	0.94840
H	5.42010	-1.59840	-1.11860
H	3.40490	-2.22350	-2.49050
H	2.97900	1.95060	-2.70850

***N*-((trifluoromethyl)sulfonyl)formimidamide (I)**

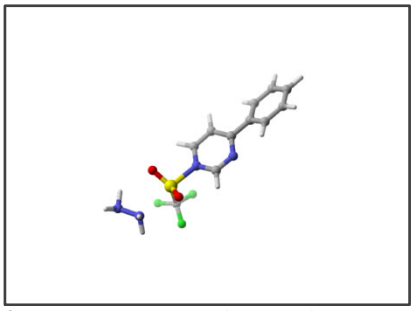


Solution phase energy (Hartrees) = -1036.06435

N	1.49370	1.23240	-0.25430
C	1.29020	2.53890	-0.74070
N	2.13610	3.24920	-1.36450
S	0.28760	0.29540	0.40370
O	0.91730	-0.78880	1.14800
O	-0.71640	1.17970	0.98740
C	-0.52450	-0.47680	-1.10150
F	-0.88640	0.49640	-1.93890
F	0.33670	-1.29360	-1.70310
F	-1.59760	-1.15850	-0.70680
H	0.29940	2.92740	-0.50970
H	2.36290	0.74140	-0.44810
H	3.02470	2.76140	-1.51130

Transition State 2a

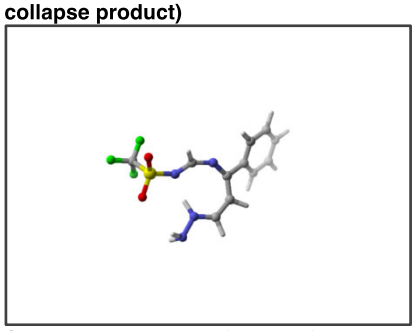
detriflylation of N-triflylpyrimidinium intermediate



Solution phase energy (Hartrees) = -1494.044267

C	-0.30710	-2.94290	1.44330
N	0.33440	-2.05710	2.23900
C	1.04960	-1.04740	1.70000
N	1.12790	-0.84570	0.40790
C	0.46980	-1.67720	-0.43010
C	-0.24350	-2.78430	0.07540
C	0.51310	-1.32420	-1.86050
C	0.74500	0.01580	-2.21740
C	0.75110	0.39300	-3.55710
C	0.55020	-0.56650	-4.55260
C	0.33540	-1.90310	-4.20440
C	0.30430	-2.28370	-2.86350
N	-0.03550	-2.10140	6.70220
N	-0.99890	-3.02930	7.23030
S	0.06540	-2.05040	4.16320
O	0.38030	-0.66370	4.38700
O	-1.21170	-2.71540	4.21970
C	1.50110	-3.25270	4.55880
F	2.00910	-3.69820	3.42520
F	2.40790	-2.58570	5.23200
F	1.00620	-4.24860	5.25230
H	-0.87460	-3.73930	1.92230
H	1.57030	-0.37250	2.37630
H	-0.78250	-3.47600	-0.56470
H	0.90200	0.75850	-1.44160
H	0.91200	1.43430	-3.82330
H	0.56230	-0.27230	-5.59950
H	0.19270	-2.64910	-4.98060
H	0.15120	-3.33010	-2.60920
H	-0.35450	-1.13640	6.81490
H	0.82240	-2.17150	7.25330
H	-1.50280	-3.42350	6.43610
H	-1.69170	-2.52740	7.79040

(*Z*)-*N'*-((1*Z*,3*E*)-3-hydrazineylidene-1-phenylprop-1-en-1-yl)-*N*-((trifluoromethyl)sulfonyl)formimidamide (aminal collapse product)

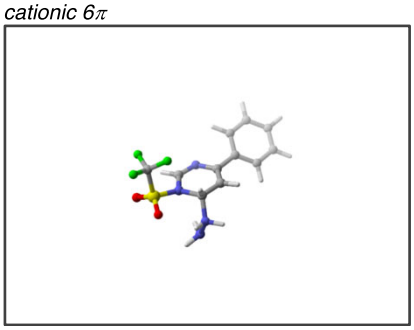


Solution phase energy (Hartrees) = -2568.06969

C	-0.11590	0.55360	2.05090
N	-3.18010	1.79820	3.11130
C	-3.51000	1.49710	1.85220
N	-3.21480	0.38130	1.26260
C	-2.30320	-0.57040	1.31780
C	-0.90380	-0.44970	1.49880
C	-2.80690	-1.92350	0.93750
C	-3.92010	-2.04600	0.10170
C	-4.38600	-3.29970	-0.26690
C	-3.75510	-4.44660	0.20360
C	-2.65930	-4.33460	1.05160
C	-2.18610	-3.08130	1.41540
N	-0.47420	1.63310	2.71180
N	0.52230	2.46510	3.25810
S	-3.54140	3.31360	3.60920
O	-2.31840	3.90430	4.14240
O	-4.37230	4.07060	2.68330
C	-4.61160	2.93070	5.06930
F	-5.68950	2.26600	4.66810
F	-3.94410	2.19270	5.94780
F	-4.98630	4.06630	5.64460
H	0.96310	0.44400	1.97120
H	-4.10580	2.20410	1.26910
H	-0.32820	-1.28010	1.11020
H	-4.40140	-1.14630	-0.26450
H	-5.24200	-3.38320	-0.92840
H	-4.11920	-5.42680	-0.08770
H	-2.17330	-5.22590	1.43470
H	-1.34620	-3.00190	2.09770
H	-1.45770	1.76020	3.00590
H	0.47120	2.37140	4.27080
H	0.23930	3.42160	3.05820

Transition state 3a

cationic 6π

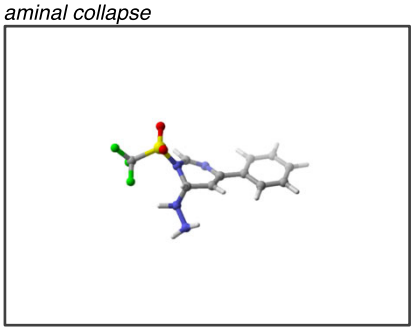


Solution phase energy (Hartrees) = -2568.00882

C	1.61720	2.28600	3.50220
N	1.38910	0.70350	3.43980
C	0.80820	0.10540	2.30140
N	0.50070	0.72860	1.24280
C	0.73870	2.11420	1.15710
C	1.26990	2.84090	2.16170
C	0.25340	2.71200	-0.11480
C	0.92670	3.76770	-0.73830
C	0.43760	4.30870	-1.92740
C	-0.73470	3.81000	-2.49710
C	-1.41300	2.75890	-1.87780
C	-0.91340	2.20070	-0.70350
N	3.05970	2.54660	3.93730
N	4.08090	1.70440	3.35840
S	1.31560	-0.14690	4.87310
O	1.53150	-1.54320	4.58960
O	2.09190	0.61700	5.82620
C	-0.48080	0.01770	5.35530
F	-1.18020	-0.91240	4.73400
F	-0.58680	-0.12580	6.65720
F	-0.91610	1.21710	4.99500
H	1.01680	2.72080	4.30580
H	0.64730	-0.97170	2.37660
H	1.35680	3.92190	2.07730
H	1.85070	4.14910	-0.31150
H	0.97830	5.11420	-2.41660
H	-1.11630	4.23480	-3.42230
H	-2.32960	2.36930	-2.31400
H	-1.44130	1.37700	-0.23200
H	3.27440	3.53440	3.70710
H	3.11430	2.51960	4.96940
H	4.50580	1.15920	4.11710
H	3.64900	1.03200	2.71890

Transition state 3b

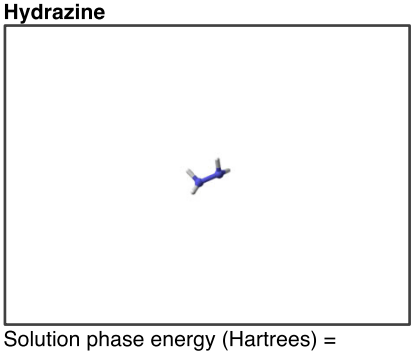
aminal collapse



Solution phase energy (Hartrees) = -2568.05178

C	2.61430	1.06750	3.70880
N	3.80120	0.88270	2.86210
C	4.10420	1.94040	1.98110
N	3.21580	2.73260	1.53490
C	1.86670	2.42190	1.80810
C	1.53160	1.59790	2.81310
C	0.89870	2.99730	0.84430
C	-0.47910	2.96540	1.08380
C	-1.37100	3.44980	0.13780
C	-0.90060	3.98550	-1.05800
C	0.46780	4.04200	-1.29460
C	1.36200	3.55340	-0.35050
N	2.98640	2.03830	4.74180
N	1.84390	2.40170	5.58320
S	4.64120	-0.54680	2.78000
O	3.76760	-1.63660	3.15620
O	5.42220	-0.52600	1.56410
C	5.84320	-0.35500	4.18040
F	5.16350	-0.24860	5.32270
F	6.63540	-1.40970	4.23980
F	6.56070	0.74220	3.99640
H	2.33070	0.08380	4.10570
H	5.14760	2.04890	1.70470
H	0.51220	1.27640	2.98410
H	-0.86390	2.57250	2.01920
H	-2.43690	3.41370	0.33770
H	-1.59870	4.36210	-1.79820
H	0.84520	4.46560	-2.21980
H	2.42930	3.59500	-0.53140
H	3.67440	1.58400	5.33860
H	2.04250	2.05880	6.52140
H	1.03850	1.85140	5.28630

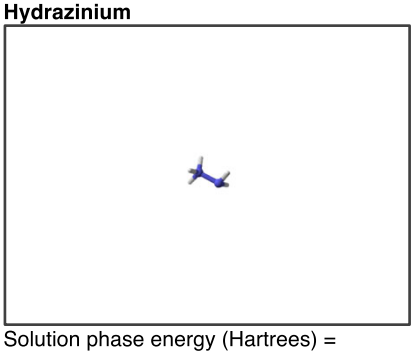
Hydrazine



Solution phase energy (Hartrees) =
-111.96323

N	0.53990	0.47720	0.04420
N	-0.53990	-0.47720	0.04420
H	1.40580	-0.01760	0.25880
H	0.67150	0.90940	-0.87250
H	-0.67150	-0.90940	-0.87250
H	-1.40580	0.01760	0.25880

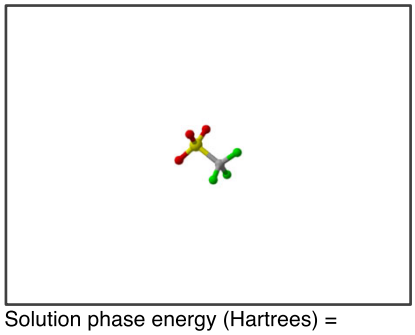
Hydrazinium



Solution phase energy (Hartrees) =
-112.408097

N	0.58940	0.45890	0.12420
N	-0.52160	-0.46240	0.05710
H	1.44910	-0.09220	0.04090
H	0.54060	1.05840	-0.70510
H	-0.55430	-1.02330	-0.80550
H	-1.40640	0.05830	0.13910
H	-0.48370	-1.10610	0.86020

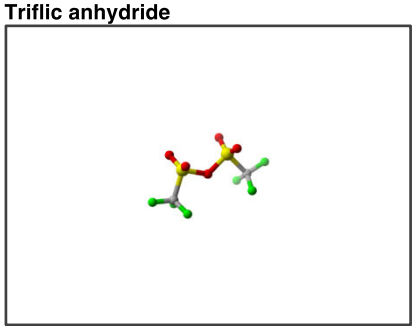
Triflate



Solution phase energy (Hartrees) =
-961.98883

S	-0.13670	0.91570	0.00000
O	1.22980	1.46330	0.00000
O	-0.89430	1.14540	-1.24100
O	-0.89430	1.14540	1.24100
C	0.13510	-0.90700	0.00000
F	0.82120	-1.28430	-1.07910
F	-1.02730	-1.56010	0.00000
F	0.82120	-1.28430	1.07910

Triflic anhydride



Solution phase energy (Hartrees) =
-1848.28160

S	3.68230	0.05010	1.07440
O	2.69650	0.68720	1.90220
O	4.34970	-1.16810	1.44070
C	4.95140	1.31460	0.53420
F	4.32760	2.36190	0.03670
F	5.63570	1.64880	1.61120
F	5.74200	0.77080	-0.36720
S	1.79250	-1.09460	-0.86100
O	3.07100	-0.11350	-0.46090
O	0.59660	-0.56930	-0.26330
O	2.20180	-2.46530	-0.73020
C	1.85470	-0.59700	-2.66350
F	1.65660	0.70120	-2.75710
F	3.02900	-0.92680	-3.15930
F	0.89010	-1.25910	-3.27270

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