---Electronic supplementary information---

Palladium-Catalyzed Remote C–H Functionalization of 2-Aminopyrimidines

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Table of Content

1. General Considerations

Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. Non-halogenated solvents were dried over calcium hydride. All the solvents were degassed with argon and stored over activated molecular sieves (4 Å).

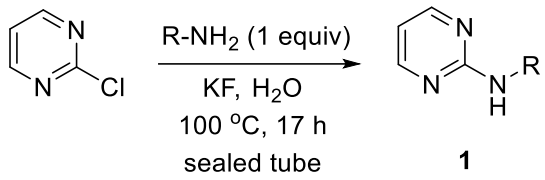
Analytical: ^{1}H, ^{13}C {1H}, ^{19}F NMR spectra were collected using Bruker (^{1}H: 500 MHz, ^{13}C {1H}: 126 MHz) and JEOL (^{1}H: 400 MHz, 13C {1H}: 100 MHz) and were referenced to the resonances of the solvent used. Coupling constants (*J*) are reported in Hertz (Hz). Coupling patterns are indicated as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), or m (multiplet). Mass spectra were recorded on Bruker micrOTOF-Q II spectrometer. FT-IR spectra were recorded by Perkin–Elmer FT–IR Spectrometer. For thin-layer chromatography (TLC) analysis Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), KMnO4, and ceric ammonium molybdate strain.

Chemicals: Commercially available chemicals were purchased from Sigma–Aldrich, Combi-Blocks, TCI, Alfa–Aesar, and Avra Synthesis and used without further purification. 2-Aminopyrimidines were prepared by following the literature procedures.[1]

2. Experimental Section

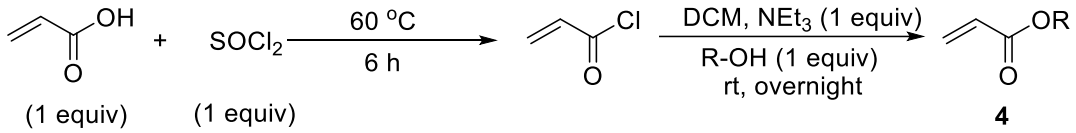
2a. General procedure

General Procedure A (GP A): General procedure for synthesizing *N*-(alkyl)pyrimidin-2-amine[1]



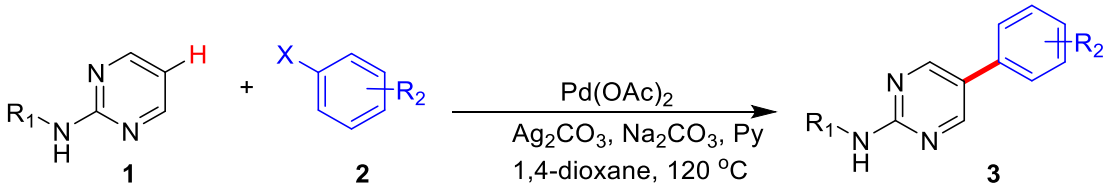
To a 15 mL sealed tube was added 2-chloropyrimidine (4 mmol), amine (4 mmol), potassium fluoride (8 mmol), in solvent (2.5 mL) and the resulting mixture heated to 100 °C for 17 h on an oil bath. Once cooled, the mixture was quenched with aqueous potassium carbonate solution (40 mL) and extracted into ethyl acetate (2 x 30 mL). The organic extracts were then combined and washed with brine before being dried over sodium sulfate and the solvent evaporated under reduced pressure. The purification was carried out by column chromatography over silica gel. Yields are not optimized.

General Procedure B (GP B): General procedure for synthesizing olefins[2]



In a round bottom flask, acrylic acid (1 equiv, 3 mmol) was taken and cooled at 0° C, then $SOCl_2$ (1 equiv, 3 mmol) was added, and stirred at 60° C for 6 h. After that DCM (3 ml) was added followed by Et_3N (1 equiv, 3 mmol) and substituted benzyl alcohol (1 equiv, 3 mmol) at 0° C. The reaction was allowed to stir at room temperature overnight. To the reaction mixture, brine solution (5 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 x 6 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The remaining residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired acrylate. Yields are not optimized. **4e-k** were synthesized using above mentioned procedure.

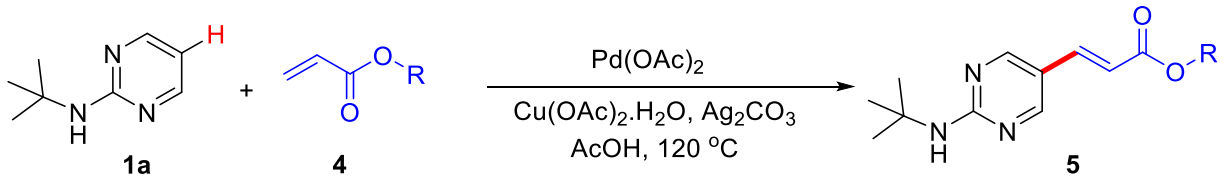
General Procedure C (GP C): General procedure for C-5 arylation



An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, 2-aminopyrimidine substrate **1** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol%, 0.02 mmol, 4.6 mg), Na_2CO_3 (0.4 mmol, 2 equiv, 42 mg), Ag_2CO_3 (0.4 mmol, 2 equiv, 110 mg) and pyridine (20 mol%, 0.04 mmol, 4 µL) were

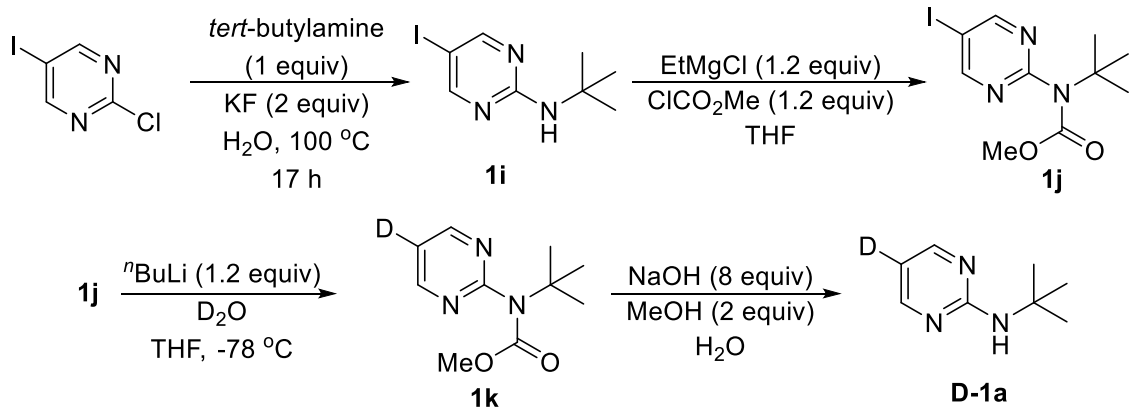
taken in air. Subsequently, Dioxane (1 mL) and aryl halide **2** (0.6 mmol, 3 equiv) were added. The reaction tube was capped tightly and placed on a preheated oil bath at 120 °C. The reaction mixture was stirred vigorously for 17 h. After that the resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The purification was carried out by column chromatography over silica gel (hexane/EtOAc) to give the C-H arylated product **3**.

General Procedure D (GP D): General procedure for C-5 olefination



An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, *N*-(tertbutyl)pyrimidin-2-amine **1a** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol%, 0.01 mmol, 4.6 mg), $Cu(OAc)_2.H_2O$ (0.2 mmol, 2 equiv, 80 mg), Ag_2CO_3(0.2 mmol, 2 equiv, 110 mg) were taken in air. Subsequently, AcOH (1 mL) and olefin **4** (0.3 mmol, 3 equiv) were added. The reaction tube was capped tightly and placed on a preheated oil bath at 120 °C. The reaction mixture was stirred vigorously for 30 h. Once cooled, the mixture was quenched with aqueous sodium chloride solution (15 mL) and extracted into ethyl acetate (2 x 30 mL), the organic part was then passed through sodium sulfate and the solvent evaporated under reduced pressure. The purification was carried out by column chromatography over silica gel (Hexane/EtOAc) to give the C-H olefinated product **5**.

2b. procedure for synthesis of deuteriated-1a



To a 15 mL sealed tube was added 2-chloro-5-iodopyrimidine (2 mmol, 480 mg), *tert*-butylamine (2 mmol, 210 µL), potassium fluoride (4 mmol, 232 mg), in solvent (1.5 mL) and the resulting mixture heated to 100 °C for 17 h on a heating block. Once cooled, the mixture was quenched with aqueous potassium carbonate solution (40 mL) and extracted into ethyl acetate (2 x 30 mL). The organic extracts were then combined and washed with brine before being dried over sodium sulfate and the

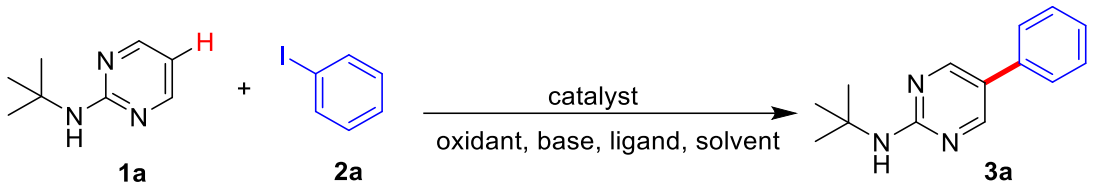
solvent evaporated under reduced pressure. The purification was carried out by column chromatography over silica gel and **1i** was obtained (454 mg, 82%) as white solid.

To an oven dried round bottom flask were added **1i** (1.64 mmol, 454 mg), THF (15 mL) under nitrogen. The solution was cooled to 0 ^{o}C and EtMgCl (2 M, 1 mL) was added slowly, after addition the solution was kept at room temperature and stirred overnight. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and water and dried over Na_2SO_4, filtered and concentrated. The product **1j** was purified using column chromatography over silica gel (hexane/ EtOAc = 10:1) to give yellow oil (467, 85%).

To an oven dried two neck round bottom flask were added **1j** (0.7 mmol, 235 mg) and THF (10 mL) under nitrogen condition, the solution was cooled to -78 ^{o}C and ^{n}BuLi (0.5 mL, 2.5 M in THF) was added slowly. After stirring for one hour, D_2O (0.3 mL) was added to the reaction mixture. After stirring for two hours the reaction mixture was allowed to warm to room temperature. The mixture was diluted with ethyl acetate, washed with water, dried over Na_2SO_4, concentrated. The product was purified with silica gel chromatography (hexane/ EtOAc = 20:1) to give **1k** as a yellow oil (130 mg, 88%). Next the deprotection of **1k** was carried out. To an oven dried round bottom flask **1k** (0.6 mmol, 130 mg), 10% of aq. NaOH (8 equiv) and methanol (2 equiv) were refluxed for overnight. After cooling to room temperature, the product was extracted into ethyl acetate, dried over Na_2SO_4, filtered and concentrated. The product **D-1a** was purified using column chromatography over silica gel to give a white solid (56 mg, 61%).

2c. Optimization of C5-arylation

Table S1: Initial finding

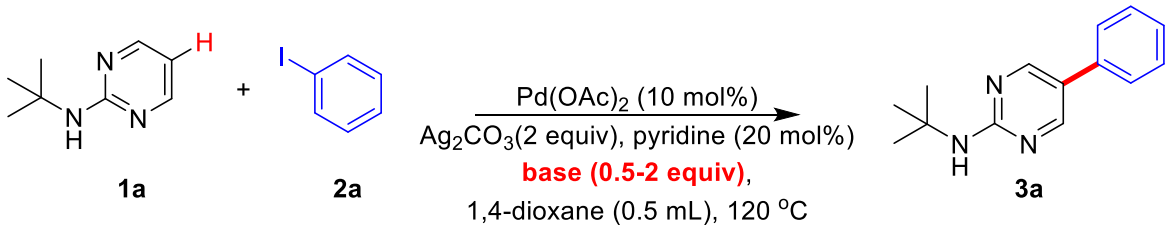


1a + **2a** → **3a**

#	Catalyst	Oxidant	Base	Ligand	Solvent	Yield (%)[a]
1	$Cu(OAc)_2$	Ag_2CO_3	Na_2CO_3	-	Toluene	N.D
2	$Fe(acac)_3$	Ag_2CO_3	Na_2CO_3	-	Toluene	N.D
3	$Ni(OAc)_2.4H_2O$	Ag_2CO_3	Na_2CO_3	-	Toluene	N.D
4	$Cu(OAc)_2$	Ag_2CO_3	Na_2CO_3	-	Toluene	N.D
5	$Pd(OAc)_2$	Ag_2CO_3	Na_2CO_3	-	Toluene	20%
6	$Pd(OAc)_2$	Ag_2CO_3	Na_2CO_3	-	Dioxane	62%
7	**$Pd(OAc)_2$**	**Ag_2CO_3**	**Na_2CO_3**	**Pyridine**	**Dioxane**	**77%**

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (10 mol%), Ag_2CO_3 (0.2 mmol), Na_2CO_3 (0.2 mmol), solvent (0.5 mL), under air at 120 °C for 17h. Isolated yield.

Table S2: Optimization of base and loading of base

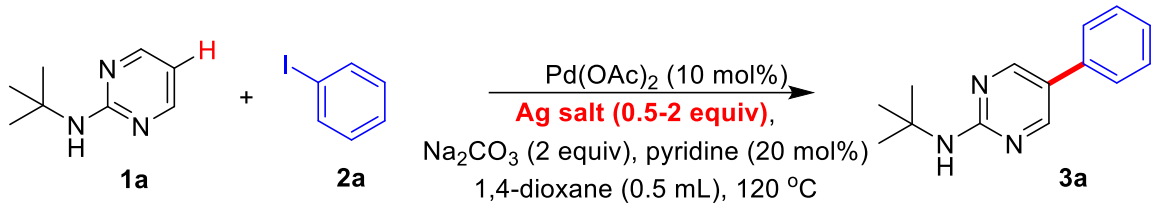


1a + **2a** → **3a**

#	Base	Yield (%)[a]
1	**Na_2CO_3 (2 equiv)**	**77% (85%)[b]**
2	K_2CO_3 (2 equiv)	66%
3	K_3PO_4 (2 equiv)	33%
4[b]	Na_2CO_3 (1.5 equiv)	68%
5[b]	Na_2CO_3 (1 equiv)	55%
6[b]	Na_2CO_3 (0.5 equiv)	46%

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.2 mmol), base (0.05 - 0.2 mmol), pyridine (20 mol%) dioxane (0.5 mL), under air at 120 °C for 17h. Isolated yield.
[b]GC yield of crude reaction mixture using mesitylene as an internal standard.

Table S3: Optimization of Ag salt and loading of Ag salt



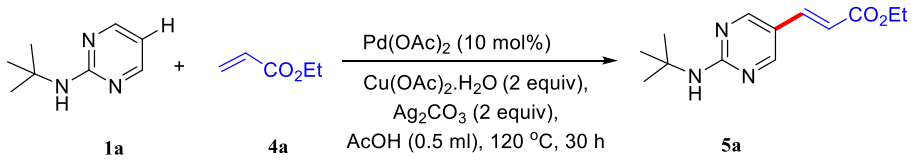
1a 2a 3a

#	Base	Yield (%)[a]
1	**Ag_2CO_3 (2equiv)**	**77%(85%)[b]**
2	AgOAc (2 equiv)	28%
3	$AgNO_3$ (2 equiv)	15%
4[b]	Ag_2CO_3 (1.5 equiv)	68%
5[b]	Ag_2CO_3 (1 equiv)	57%
6[b]	Ag_2CO_3 (0.5 equiv)	50%

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Na_2CO_3 (0.2 mmol), oxidant (0.05 - 0.2 mmol), pyridine (20 mol%) dioxane (0.5 mL), under air at 120 °C for 17h. Isolated yield. [b]GC yield of crude reaction mixture using mesitylene as an internal standard.

2d. Optimization of selective olefination

Table S4: Initial finding[a]

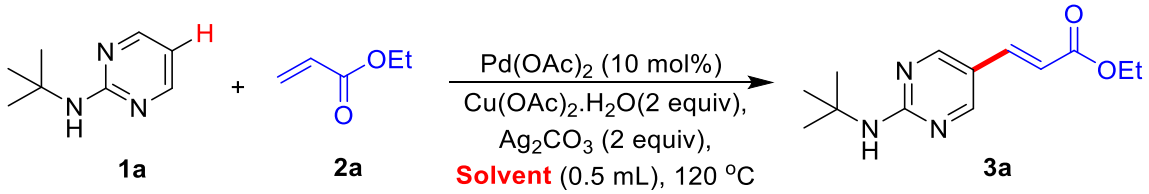


1a 4a 5a

Entry	Variations from standard condition	**5a** (%)[a]
1	None	**75%**
2	No $Pd(OAc)_2$	N.D
3	No $Cu(OAc)_2.H_2O$	N.D
4	Na_2CO_3 instead of Ag_2CO_3	N.D
5	O_2 instead of Ag_2CO_3	38%
6	$Cu(OAc)_2$ instead of $Cu(OAc)_2.H_2O$	65%
7	in Dioxane	10%
8	in PivOH	40%
9	in DMA	10%
10	at 90 °C	trace

[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.2 mmol), AcOH (0.5 mL), under air at 120 °C for 30h. Isolated yield.

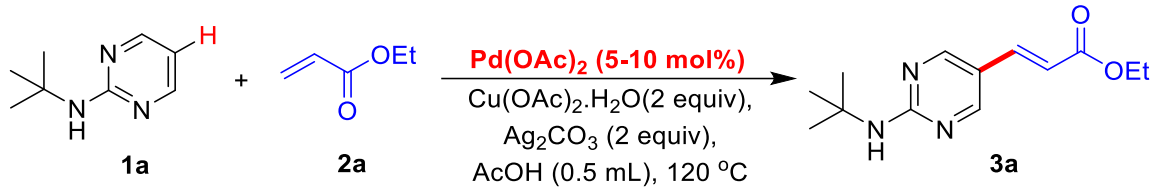
Table S5: Optimization of solvent



#	solvent	Yield (%)[a]
1	DMF	30%
2	DMA	10%
3	PivOH	40%
4	**AcOH**	**75%**
5	AcOH:DMA	47%
6	Dioxane	10%

[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.2 mmol), solvent (0.5 mL), under air at 120 °C for 30h. Isolated yield.

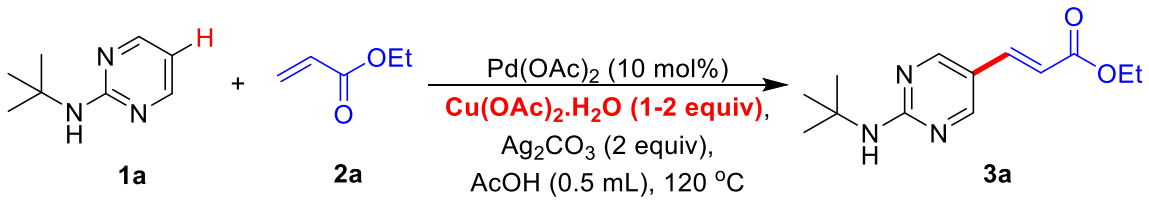
Table S6: Optimization of catalyst loading



#	**$Pd(OAc)_2$**	**Yield (%)[a]**
1	**10 mol%**	**75%**
2	5 mol%	30%

[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.3 mmol), $Pd(OAc)_2$ (5-10 mol%), Ag_2CO_3 (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.2 mmol), AcOH (0.5 mL), under air at 120 °C for 30h. Isolated yield.

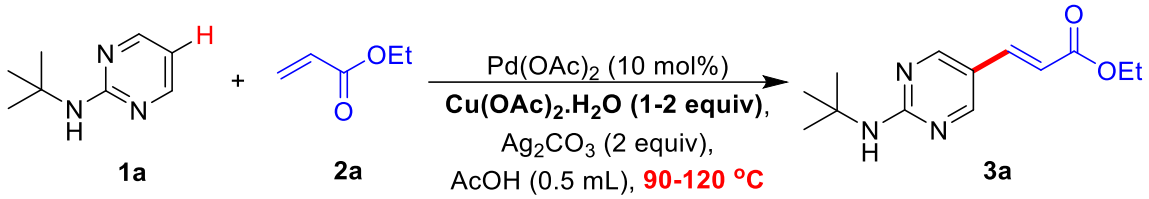
Table S7: Optimization of Cu salt loading



#	**$Cu(OAc)_2.H_2O$**	**Yield (%)[a]**
1	**2 equiv**	**75%**
2	1.5 equiv	43%
3	1 equiv	31%

[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.1-0.2 mmol), AcOH (0.5 mL), under air at 120 °C for 30h. Isolated yield.

Table S8: Optimization of temperature

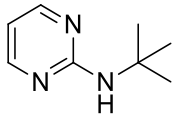


#	temperature	Yield (%)[a]
1	**120° C**	**75%**
2	110° C	65%
3	100° C	32%
4	90° C	trace

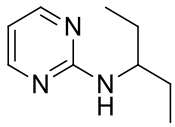
[a]Reaction conditions: **1a** (0.1 mmol), **4a** (0.3 mmol), $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.2 mmol), $Cu(OAc)_2.H_2O$ (0.2 mmol), AcOH (0.5 mL), under air at 90-120 °C for 30h. Isolated yield.

3. Characterisation of the synthesised compounds

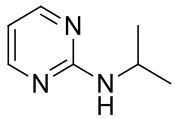
3a. Characterisation of substrates



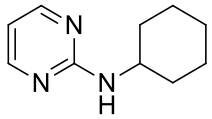
N-(tert-butyl)pyrimidin-2-amine (1a):[3] According to GP A in 5 mmol scale, 665 mg, 88%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.23 (d, *J* = 4.7 Hz, 2H), 6.46 (t, *J* = 4.8 Hz, 1H), 5.12 (s, 1H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.3, 157.6, 110.1, 50.9, 28.9.



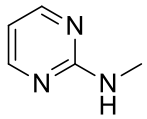
N-(pentan-3-yl)pyrimidin-2-amine (1b): According to GP A in 2 mmol scale, 280 mg, 85%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.22 (d, *J* = 4.6 Hz, 2H), 6.45 (t, *J* = 4.8 Hz, 1H), 5.30 (d, *J* = 7.2 Hz, 1H), 3.88 (dd, *J* = 7.3, 1.7 Hz, 1H), 1.67 – 1.57 (m, 2H), 1.53 – 1.43 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.6, 158.0, 110.0, 53.4, 27.2, 10.2. For $C_8H_{12}IN_3$ $[M+H]^+$: 165.1266. Found: 165.1265



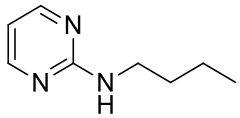
N-isopropylpyrimidin-2-amine (1c):[4] According to GP A in 2 mmol scale, 236 mg, 86%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.25 (d, *J* = 4.7 Hz, 4H), 6.48 (d, *J* = 4.8 Hz, 2H), 4.12 (d, *J* = 7.4 Hz, 2H), 1.23 (d, *J* = 6.5 Hz, 13H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.9, 158.2, 110.3, 42.9, 23.0.



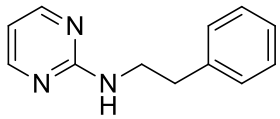
N-cyclohexylpyrimidin-2-amine (1d):[1] According to GP A in 2 mmol scale, 276 mg, 78%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.22 (d, *J* = 4.7 Hz, 2H), 6.44 (t, *J* = 4.8 Hz, 1H), 5.27 (d, *J* = 4.3 Hz, 1H), 3.79 (ddd, *J* = 10.4, 9.3, 4.3 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.76 – 1.68 (m, 2H), 1.65 – 1.57 (m, 1H), 1.39 (dd, *J* = 20.8, 7.7 Hz, 2H), 1.21 (dd, *J* = 16.9, 8.0 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.9, 158.1, 110.2, 49.7, 33.4, 25.9, 25.0.



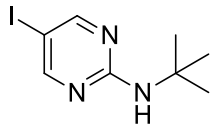
N-methylpyrimidin-2-amine (1e):[5] According to GP A in 2 mmol scale, 179 mg, 82%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.26 (d, *J* = 4.7 Hz, 2H), 6.49 (t, *J* = 4.8 Hz, 1H), 5.43 (s, 1H), 2.99 – 2.96 (m, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 163.1, 158.1, 110.4, 28.4.



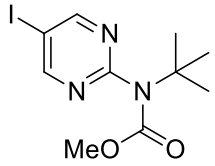
N-butylpyrimidin-2-amine (1f):[6] According to GP A in 2 mmol scale, 230 mg, 76%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.25 (d, *J* = 4.7 Hz, 2H), 6.48 (t, *J* = 4.8 Hz, 1H), 5.30 (s, 1H), 3.38 (td, *J* = 7.2, 5.9 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.40 (dd, *J* = 15.2, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 162.6, 158.1, 110.4, 41.3, 31.8, 20.2 13.9.



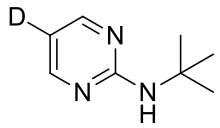
N-phenethylpyrimidin-2-amine (1g):[7] According to GP A in 2 mmol scale, 310 mg, 78%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.27 (d, *J* = 4.7 Hz, 4H), 7.33 – 7.27 (m, 5H), 7.23 (d, *J* = 7.5 Hz, 7H), 6.52 (t, *J* = 4.8 Hz, 2H), 5.18 (s, 2H), 3.77 – 3.63 (m, 5H), 2.92 (t, *J* = 7.0 Hz, 5H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.4, 158.2, 139.4, 129.0, 128.7, 126.5, 110.7, 42.7, 35.9. For $C_{12}H_{13}N_3$ $[M+H]^+$: 199.1109. Found: 199.1107.



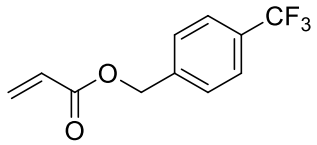
N-(tert-butyl)-5-iodopyrimidin-2-amine (1i): ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.33 (s, 2H), 5.17 (s, 1H), 1.41 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.5, 160.3, 75.9, 51.2, 28.8. For $C_8H_{12}IN_3$ $[M+H]^+$: 277.0076. Found: 277.0064.



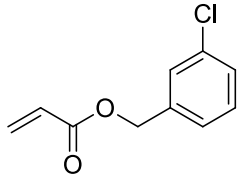
methyl tert-butyl(5-iodopyrimidin-2-yl)carbamate (1j): ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.91 (s, 2H), 3.57 (s, 3H), 1.40 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 164.2, 159.8, 154.6, 91.4, 58.2, 52.6, 28.8. **HRMS** calcd. For $C_{10}H_{14}IN_3O_2$ $[M+H]^+$: 336.0203. Found: 336.0201.



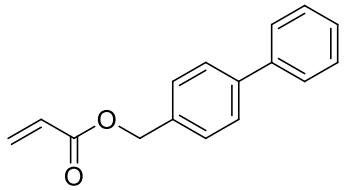
(D-1a): ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.22 (d, *J* = 2.9 Hz, 2H), 6.46 (t, *J* = 4.8 Hz, 0.3H), 5.12 (s, 1H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.3, 157.6, 110.2, 50.9, 29.0. For $C_8H_{12}DN_3$ $[M+H]^+$:153.1245. Found: 153.1255.



4-(trifluoromethyl)benzyl acrylate (4e)[8]: According to GP B in 3 mmol scale, 386 mg, 56%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 6.51 – 6.44 (m, 1H), 6.19 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.91 – 5.87 (m, 1H), 5.26 (s, 2H).

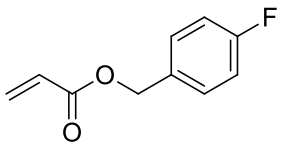


4-chlorobenzyl acrylate (4f): According to GP B in 3 mmol scale, 306 mg, 52%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 7.34 (s, 1H), 7.27 (dd, *J* = 3.8, 1.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.44 (dd, *J* = 17.5, 1.3 Hz, 1H), 6.15 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.87 – 5.83 (m, 1H), 5.14 (s, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 165.9, 138.3, 137.4, 137.1, 131.5, 130.4, 128.2, 127.4, 94.4, 77.4, 77.1, 76.9, 65.3.

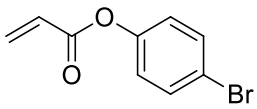


[1,1'-biphenyl]-4-ylmethyl acrylate (4g)[9]: According to GP B in 3 mmol scale, 421 mg, 59%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 7.60 (dd, *J* = 7.6, 5.1 Hz, 4H), 7.46 (d, *J* = 8.9 Hz, 4H), 7.37

(d, *J* = 7.5 Hz, 1H), 6.51 – 6.45 (m, 1H), 6.19 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.89 – 5.84 (m, 1H), 5.25 (s, 2H).

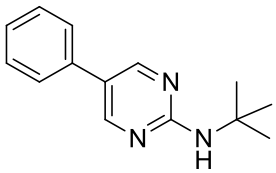


4-fluorobenzyl acrylate (4h)[10]: According to GP B in 3 mmol scale, 330 mg, 61%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 7.48 – 7.30 (m, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 6.44 (dd, *J* = 17.5, 1.3 Hz, 1H), 6.15 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.85 (dd, *J* = 10.6, 1.3 Hz, 1H), 5.16 (s, 2H).

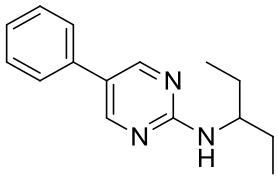


4-bromophenyl acrylate (5k): According to GP B in 3 mmol scale, 391mg, 58%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 7.59 – 7.42 (m, 2H), 7.09 – 6.94 (m, 2H), 6.65 – 6.57 (m, 1H), 6.31 (dd, *J* = 17.2, 10.3 Hz, 1H), 6.03 (d, *J* = 10.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.2, 149.7, 133.1, 132.5, 127.7, 123.4, 119.0, 77.4, 77.1, 76.9.

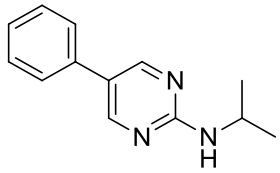
3b. Characterisation of products



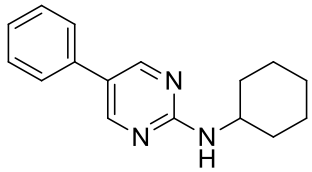
N-(tert-butyl)-5-phenylpyrimidin-2-amine (3a): According to GP C, 35 mg, 77%. **IR:** 2920.6, 1605.8, 1521.9, 1452.4, 1383.0, 801.6, 757.2, 694.7**. ^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.50 (s, 2H), 7.49 – 7.41 (m, 3H), 7.33 (t, *J* = 7.1 Hz, 1H), 5.24 (s, 1H) 1.48 (s, 9H).**^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.4, 155.9, 136, 129.2, 127.3, 125.9, 123.4, 51.2, 29.1. **HRMS** calcd. for $C_{14}H_{18}N_3[M+H]^+$: 228.1495. Found: 228.1495.



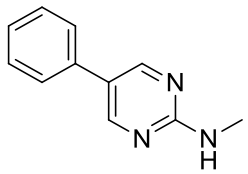
N-(pentan-3-yl)-5-phenylpyrimidin-2-amine (3b): According to GP C, 38 mg, 79%. **IR:** 2961.0, 1603.6, 1523.1, 1454.0, 1431.0, 1382.0, 1299.0, 800.2, 695.8. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.50 (s, 2H), 7.45 (d, *J* = 27.3 Hz, 4H), 7.33 (d, *J* = 16.5 Hz, 1H), 5.04 (d, *J* = 8.2 Hz, 1H), 3.95 (d, *J* = 34.4 Hz, 1H), 1.66 (d, *J* = 41.8 Hz, 2H), 1.52 (d, *J* = 43.4 Hz, 2H), 0.96 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 162.1, 156.4, 135.9, 129.2, 127.3, 125.9, 123.9, 53.7, 27.3, 10.3. **HRMS** calcd. for $C_{15}H_{20}N_3[M+H]^+$: 242.1652. Found: 242.1656.



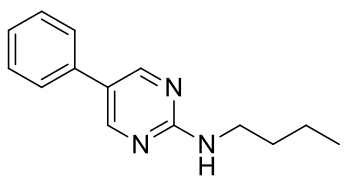
N-isopropyl-5-phenylpyrimidin-2-amine (3c): According to GP C, 31 mg, 72%. **IR:** 2926.7, 1603.0, 1522.4, 1454.5, 1378.2, 1236.2, 1119.4, 801.2, 754.6, 695.2, 512.8. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.51 (s, 2H), 7.45 (dt, *J* = 15.2, 7.5 Hz, 4H), 7.34 (t, *J* = 7.1 Hz, 1H), 5.14 (d, *J* = 6.4 Hz, 1H), 4.18 (td, *J* = 13.0, 6.5 Hz, 1H), 1.29 (s, 3H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.2, 156.4, 135.8, 129.3, 127.4, 126.0, 123.7, 43.2, 23.1. **HRMS** calcd. for $C_{13}H_{16}N_3$ $[M+H]^+$: 214.1339. Found: 214.1334.



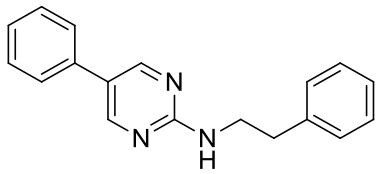
N-cyclohexyl-5-phenylpyrimidin-2-amine (3d): According to GP C, 32 mg, 64%. **IR:** 2922.4, 1607.3, 1522.4, 1554.5, 1297.6, 1236.2, 1166.0, 1072.7, 795.9, 754.5, 695.2 **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.51 (s, 2H), 7.44 (dt, *J* = 15.1, 7.6 Hz, 4H), 7.33 (t, *J* = 7.0 Hz, 1H), 5.24 (d, *J* = 7.4 Hz, 1H), 3.94 – 3.80 (m, 1H), 2.12 – 2.02 (m, 2H), 1.77 (dd, *J* = 9.6, 3.9 Hz, 2H), 1.65 (dd, *J* = 9.1, 3.8 Hz, 1H), 1.51 – 1.38 (m, 2H), 1.30 – 1.25 (m, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 160.8, 156, 135.4, 128.8, 126.9, 125.5, 123.2, 49.5, 33, 25.4, 24.6. **HRMS** calcd. for $C_{16}H_{20}N_3$$[M+H]^+$: 254.1652. Found: 254.1657.



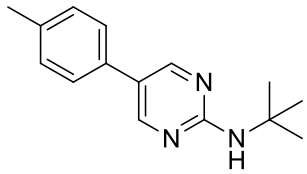
N-methyl-5-phenylpyrimidin-2-amine (3e): According to GP C, 16 mg, 42%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.54 (s, 2H), 7.50 – 7.41 (m, 4H), 7.37 – 7.31 (m, 1H), 5.19 (s, 1H), 3.06 (d, *J* = 5.0 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 162.4, 156.4, 135.8, 129.3, 127.5, 126.1, 123.9, 28.7. **HRMS** calcd. for $C_{11}H_{12}N_3$ $[M+H]^+$: 186.1026. Found: 186.1027.



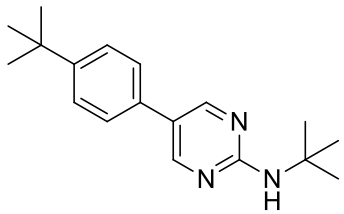
N-butyl-5-phenylpyrimidin-2-amine (3f)[6]: According to GP C, 22 mg, 48%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.52 (s, 7H), 7.50 – 7.41 (m, 16H), 7.35 (d, *J* = 6.9 Hz, 4H), 5.19 (s, 4H), 3.46 (td, *J* = 7.0, 5.9 Hz, 8H), 1.64 (dd, *J* = 7.2, 2.4 Hz, 10H), 1.44 (dd, *J* = 15.1, 7.4 Hz, 9H), 0.97 (t, *J* = 7.3 Hz, 12H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.9, 156.4, 135.8, 129.3, 127.4, 126.0, 123.8, 41.6, 31.9, 20.3, 13.9. **HRMS** calcd. for $C_{14}H_{18}N_3[M+H]^+$: 228.1495. Found: 228.1487.



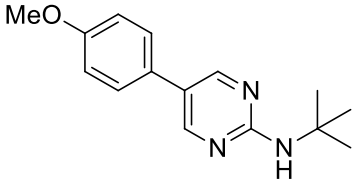
N-phenethyl-5-phenylpyrimidin-2-amine (3g): According to GP C, 21 mg, 38%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.52 (s, 2H), 7.45 (dt, *J* = 15.0, 7.6 Hz, 4H), 7.32 (dd, *J* = 14.3, 7.0 Hz, 3H), 7.26 – 7.17 (m, 3H), 5.26 (s, 1H), 3.75 (dd, *J* = 13.1, 6.6 Hz, 2H), 2.95 (t, *J* = 6.9 Hz, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.7 156.3, 139.2, 135.7, 129.2, 128.9, 128.7, 127.3, 126.5, 125.9, 123.9, 42.8, 35.8. **HRMS** calcd. for $C_{18}H_{18}N_3[M+H]^+$: 276.1495. Found: 276.1494.



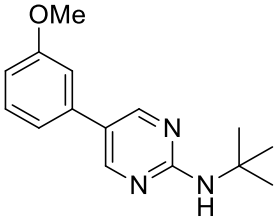
N-(tert-butyl)-5-(p-tolyl)pyrimidin-2-amine (3h): According to GP C, 33 mg, 68%. **IR:** 2965.0, 1610.8, 1531.8, 1512.4, 1445.0, 1355.6, 1284.3, 1224.7, 936.2, 817.9, 797.8, 741.7, 655.4, 638.3. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.47 (d, *J* = 1.4 Hz, 2H), 7.39 – 7.34 (m, 2), 7.25 (t, *J* = 6.1 Hz, 2H), 5.20 (s, 1H), 2.38 (s, 3H), 1.48 (d, *J* = 1.4 Hz, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.4, 155.8, 137.1, 133.1, 129.9, 125.8, 123.4, 51.1, 29.1, 21.2. **HRMS** calcd. for $C_{15}H_{20}N_3[M+H]^+$: 242.1652. Found: 242.1650.



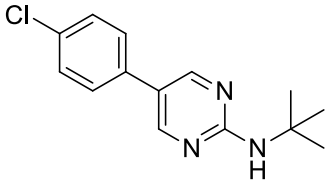
N-(tert-butyl)-5-(4-(tert-butyl)phenyl)pyrimidin-2-amine (3i): According to GP C, 39 mg, 69%. **IR:** 2964.8, 1607.3, 1509.7, 1361.2, 1225.5, 1157.6, 1115.2, 835.2, 801.2, 741.8, 572.0. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.49 (s, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.22 (s, 1H), 1.48 (s, 9H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.4, 155.8, 150.3, 133.1, 126.2, 125.6, 123.3, 51.1, 34.7, 31.5, 29.1. **HRMS** calcd. for $C_{15}H_{20}N_3O$ $[M+H]^+$:284.2121. Found: 284.2157.



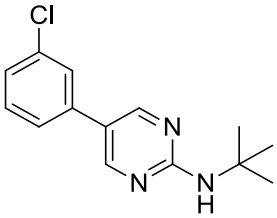
N-(tert-butyl)-5-(4-methoxyphenyl)pyrimidin-2-amine (3j): According to GP C, 31 mg, 59%. **IR:** 2964.6, 1605.0, 1596.4, 1507.3, 1453.7, 1286, 1247.6, 1225.6, 1178.9, 1034.6, 831.2, 799.6. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.44 (s, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 5.19 (s, 1H), 3.84 (s, 3H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 166.3, 159.2, 155.6, 128.5, 127.1, 123.2, 114.7, 55.5, 51.1, 29.1. **HRMS** calcd. for $C_{15}H_{20}N_3O$ $[M+H]^+$: 258.1601. Found: 258.1600.



N-(tert-butyl)-5-(3-methoxyphenyl)pyrimidin-2-amine (3k): According to GP C, 34 mg, 66%. **IR:** 2926.7, 1603.0, 1522.4, 1450.3, 1225.5, 1284.8, 1047.3, 801.2, 695.2. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.49 (s, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.87 (dd, *J* = 8.3, 2.3 Hz, 1H), 5.30 (s, 1H), 3.85 (s, 3H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.6, 160.3, 155.9, 137.4, 130.3, 123.2, 118.4, 112.6, 111.7, 55.4, 51.2, 29.1. **HRMS** calcd. for $C_{15}H_{20}N_3O$ $[M+H]^+$: 258.1601. Found: 258.1605.

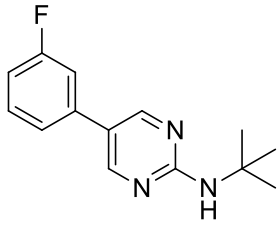


N-(tert-butyl)-5-(4-chlorophenyl)pyrimidin-2-amine (3l): According to GP C, 30 mg, 57%. **IR:** 2965.3, 1610.2, 1531.3, 1494.7, 1445.2, 1359.0, 1283.0, 1223.5, 1093.4, 798.6. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.45 (s, 2H), 7.39 (s, 4H), 5.32 (s, 1H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.6, 155.8, 134.4, 133.3, 129.4, 127.1, 122.2, 51.2, 29.0. **HRMS** calcd. for $C_{14}H_{17}ClN_3$ $[M+H]^+$: 262.1106. Found: 262.1109.

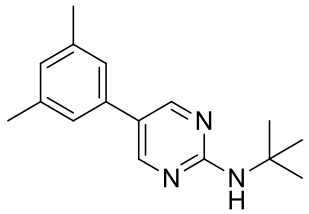


N-(tert-butyl)-5-(3-chlorophenyl)pyrimidin-2-amine (3m): According to GP C, 35 mg, 66%. **IR:** 2962.8, 1604.6, 1524.5, 1482.5, 1439.4, 1354.9, 1217.3, 762.9. **^{1}H NMR** (400 MHz,

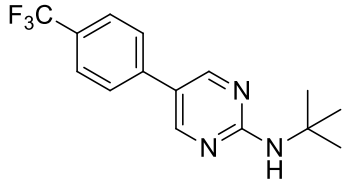
CHLOROFORM-D) δ 8.46 (s, 2H), 7.45 (s, 1H), 7.39 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 5.29 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.7, 155.9, 137.9, 135.1, 130.5, 127.3, 125.9, 123.9, 122.0, 51.3, 29.0. **HRMS** calcd. for $C_{14}H_{17}ClN_3[M+H]^+$: 262.1106. Found: 262.1084.



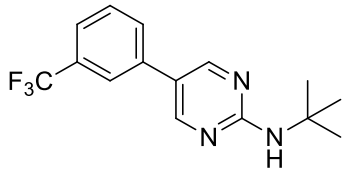
N-(tert-butyl)-5-(3-fluorophenyl)pyrimidin-2-amine (3n): According to GP C, 33.1 mg, 65%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.48 (s, 2H), 7.42-7.36 (dd, *J* = 14.7, 7.4 Hz, 1H), 7.25-7.23 (d, *J* = 7.9 Hz, 1H), 7.18-7.15 (d, *J* = 11.0 Hz, 1H), 7.03-6.99 (t, *J* = 8.3 Hz, 1H), 5.29 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 163.5 (d, *J* = 163.48 Hz), 161.7, 155.92, 138.2 (d, *J* = 8.82 Hz), 130.7 (d, *J* = 7.56), 122.2 (d, 2.52 Hz), 121.4 (d, 2.52 Hz), 114.0 (d, *J* = 20.16 Hz), 112.7 (d, 21.42 Hz), 51.2, 29.0. **^{19}F NMR** (471 MHz, CHLOROFORM-D) δ -112.3. **HRMS** calcd. for $C_{14}H_{16}FN_3[M+H]^+$: 246.1401. Found: 246.1400.



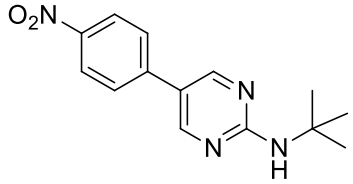
N-(tert-butyl)-5-(3,5-dimethylphenyl)pyrimidin-2-amine (3o): According to GP C, 33 mg, 65%. **IR:** 2922.4, 1603.0, 1516.2, 1361.2, 1280.6, 1221.2, 1157.6, 1030.3, 932.7, 847.8, 796.9, 699.4 **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.47 (s, 2H), 7.08 (s, 2H), 6.98 (s, 1H), 5.20 (s, 1H), 2.37 (s, 6H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.5, 155.9, 138.8, 135.9, 128.9, 123.9, 123.6, 51.1, 29.1, 21.5. **HRMS** calcd. for $C_{16}H_{22}N_3[M+H]^+$: 256.1808. Found: 256.1809.



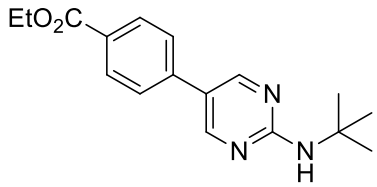
N-(tert-butyl)-5-(4-(trifluoromethyl)phenyl)pyrimidin-2-amine (3p): According to GP C, 41 mg, 68%. **IR:** 2926.7, 1603.0, 1564.8, 1323.0, 1221.2, 1170.3, 1072.7, 839.4, 741.8, 652.7. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.51 (s, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 5.36 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 161.8, 156.1, 139.6, 129.8, 129.4 (q, *J* = 33.3 Hz) 126.2 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 273.7 Hz), 121.9, 51.3, 29.0. **^{19}F NMR** (471 MHz, CHLOROFORM-D) δ -62.4. **HRMS** calcd. for $C_{15}H_{17}F_3N_3$ $[M+H]^+$: 296.1369. Found: 296.1382.



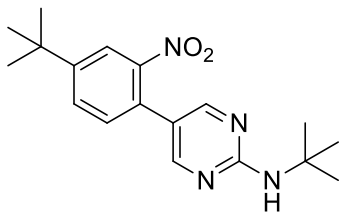
N-(tert-butyl)-5-(3-(trifluoromethyl)phenyl)pyrimidin-2-amine (3q): According to GP C, 38 mg, 65%. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.50 (s, 2H), 7.71 (s, 1H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.56 (p, *J* = 7.7 Hz, 2H), 5.33 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) 161.9, 156.0, 137.0, 131.7 (q, *J* = 32.8), 129.7, 129.1, 124.2 (q, *J* = 272.2), 123.9 (q, *J* = 3.8), 122.6 (q, *J* = 3.8), 122.1, 51.3, 29.0. **^{19}F NMR** (471 MHz, CHLOROFORM-D) δ -62.74 (s). HRMS calcd. for $C_{15}H_{17}F_3N_3[M+H]^+$: 296.1369. Found: 296.1372.



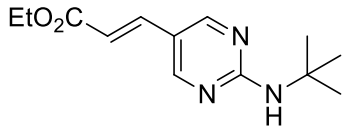
N-(tert-butyl)-5-(4-nitrophenyl)pyrimidin-2-amine (3r): According to GP C, 38 mg, 69%. **IR:** 2924.5, 1595.0, 1518.0, 1441.6, 1343, 1303.8, 1221.1, 851.6, 800.9, 751.9, 695.8. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.56 (s, 2H), 8.28 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 9.0 Hz, 2H), 5.43 (s, 1H), 1.48 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 162.0, 156.2, 146.9, 142.6, 125.9, 124.7, 120.9, 51.5, 29. HRMS calcd. for $C_{14}H_{17}N_4O_2$ $[M+H]^+$: 273.1346 . Found: 273.1345.



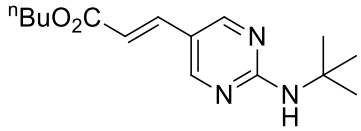
ethyl 4-(2-(tert-butylamino)pyrimidin-5-yl)benzoate (3s): According to GP C, 40 mg, 66%. **IR:** 2969.0, 1713.3, 1603.0, 1526.7, 1446.0, 1361.2, 1276.4, 1221.2, 1102.2, 1026, 852.1, 703.6. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.54 (s, 2H), 8.11 – 8.08 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 9H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 166.5, 161.8, 156.1, 140.4, 130.5, 129.2, 125.4, 122.2, 61.1, 51.3, 29.0, 14.5. **HRMS** calcd. for $C_{17}H_{22}N_3O_2[M+H]^+$: 300.1707. Found: 300.1718.



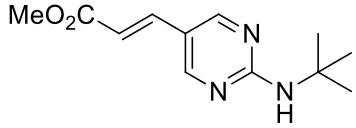
N-(tert-butyl)-5-(4-(tert-butyl)-2-nitrophenyl)pyrimidin-2-amine (3t): According to GP C, 39 mg, 60%. **IR:** 2964.8, 1603.0, 1518.2, 1433.3, 1361.2, 1276.4, 1225.5, 835.2, 741.8. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.21 (s, 2H), 7.92 (d, *J* = 1.9 Hz, 1H), 7.64 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 5.30 (s, 1H), 1.47 (s, 9H), 1.38 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 161.5, 156.7, 152.7, 148.8, 131.7, 130.1, 128.2, 121.8, 120.1, 51.3, 35.1, 31.2, 29.0. **HRMS** calcd. for $C_{18}H_{25}N_4O_2$ $[M+H]^+$: 329.1972. Found: 329.1978.



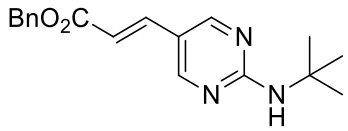
(E)-ethyl 3-(4-(2-(tert-butylamino)pyrimidin-5-yl)phenyl)acrylate (5a): According to GP D, 37.5 mg, 75%. **IR:** 2969.0, 1637.0, 1598.8, 1526.7, 1314.5, 1263.6, 1217.0, 1174.5, 1034.5, 754.6**. ^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.41 (s, 2H), 7.47 (d, *J* = 16.1 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.49 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.45 (s, 9H), 1.32 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 167.1, 162.3, 157.5, 139.2, 117.4, 114.8, 60.6, 51.6, 28.9, 14.5. **HRMS** calcd. for $C_{13}H_{20}N_3O_2$ $[M+H]^+$: 250.1550 . Found: 250.1560.



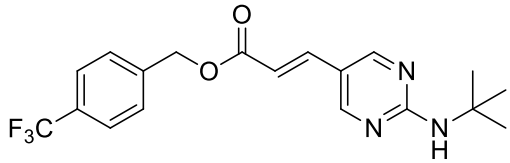
(E)-butyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5b): According to GP D, 42 mg, 76%. Yield 76% (42 mg, 0.2 mmol)**. IR:** 2960.6, 1713.3, 1598.8, 1522.4, 1454.5, 1276.4, 1221.2, 1170.3, 763.0**. ^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.41 (s, 2H), 7.47 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.28 (dd, *J* = 16.0, 1.4 Hz, 1H), 5.53 (s, 1H), 4.19 (dt, *J* = 6.8, 3.4 Hz, 2H), 1.70 – 1.65 (m, 2H), 1.45 (d, *J* = 1.3 Hz, 9H), 1.44 – 1.39 (m, 2H), 0.95 (td, *J* = 7.5, 1.3 Hz, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 167.2, 162.2, 157.4, 139.2, 117.4, 114.85, 64.5, 51.6, 30.9, 28.9, 19.3, 13.9. **HRMS** calcd. for $C_{15}H_{24}N_3O_2$ $[M+H]^+$: 278.1863. Found: 278.1896.



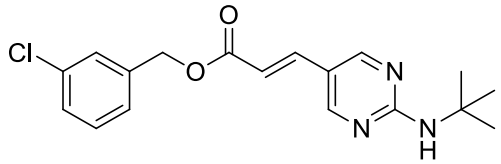
(E)-methyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5c): According to GP D, 36 mg, 77%. **IR:** 2960.6, 1721.8, 1632.7, 1603, 1531, 1361.2, 1318.8, 1221.2, 1170.3, 979.4, 796.9, 750.3, 652.7. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.41 (s, 2H), 7.48 (d, *J* = 16.1 Hz, 1H), 6.28 (d, *J* = 16.1 Hz, 1H), 5.48 (s, 1H), 3.79 (s, 3H), 1.45 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 167.5, 162.3, 157.5, 139.5, 117.4, 114.3, 51.8, 51.6, 28.9. **HRMS** calcd. for $C_{12}H_{18}N_3O_2$ $[M+H]^+$: 236.1394. Found : 236.1407.



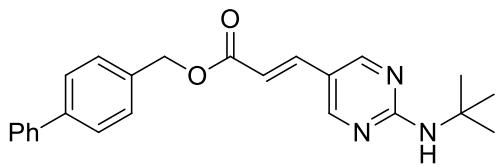
(E)-benzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5d): According to GP D, 47 mg, 76%. **IR:** 2965.0, 1712.7, 1633.6, 1597.7, 1523.9, 1455.3, 1218, 1166.3, 962.3, 749.3. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.41 (s, 2H), 7.52 (d, *J* = 16.1 Hz, 1H), 7.40 – 7.36 (m, 5H), 6.33 (d, *J* = 16.1 Hz, 1H), 5.54 (s, 1H), 5.24 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 166.9, 162.2, 157.5, 139.8, 136.2, 128.7, 128.5, 128.4, 117.3, 114.3, 66.5, 51.6, 28.9. **HRMS** calcd. for $C_{18}H_{22}N_3O_2$ $[M+H]^+$: 312.1707. Found: 312.1752.



(E)-4-(trifluoromethyl)benzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5e): According to GP D, 62 mg, 82%. **IR:** 2926.7, 1713.3, 1598.8, 1522.4, 1323.0, 1212.7, 1157.6, 1068.5, 1017.6, 983.6, 754.6. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.42 (s, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 11.2 Hz, 3H), 6.33 (d, *J* = 16.1 Hz, 1H), 5.48 (s, 1H), 5.28 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 166.7, 162.4, 157.6, 140.4, 130.5 (q, *J* = 31.5), 128.3, 125.7 (q, *J* = 3.78), 124.2 (q, *J* = 272.16), 117.2, 113.7, 65.4, 51.7, 29.1. **^{19}F NMR** (471 MHz, CHLOROFORM-D) δ -62.6. **HRMS** calcd. for $C_{19}H_{21}F_3N_3O_2$ $[M+H]^+$: 380.1580. Found: 380.1634.

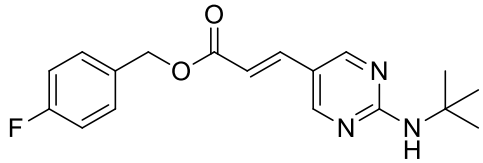


(E)-3-chlorobenzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5f): According to GP D, 41 mg, 60%. **IR:** 2965.5, 1711.5, 1597.8, 1523.6, 1457.6, 1276.0, 1215.8, 1167.8, 750.3. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.42 (s, 2H), 7.53 (d, *J* = 16.1 Hz, 1H), 7.40 (s, 1H), 7.31 (d, *J* = 5.2 Hz, 2H), 7.29 – 7.27 (m, 1H), 6.33 (d, *J* = 16.1 Hz, 1H), 5.48 (s, 1H), 5.20 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 166.7, 162.3, 157.6, 140.2, 138.3, 134.6, 130.0, 128.5, 128.4, 126.3, 117.3, 113.9, 65.5, 51.7, 28.9. **HRMS** calcd. for $C_{18}H_{21}ClN_3O_2$ $[M+H]^+$: 346.1317. Found: 346.1309.

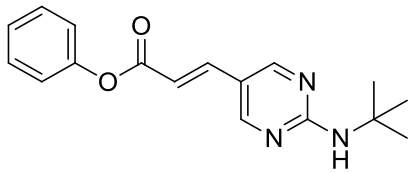


(E)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5g): According to GP D, 37 mg, 48%. **IR:** 2969.0, 1709.0, 1603.0, 1522.4, 1454.5, 1393.6, 1317.7, 1218.6, 1168.0, 984.6. 824.3, 803.2, 761.1, 697.8. 653.5. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.42 (s, 2H),

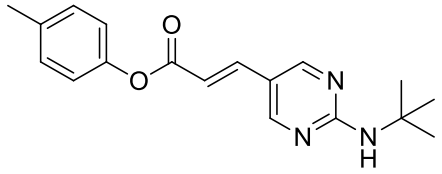
7.60 (t, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 16.1 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.35 (d, *J* = 16.1 Hz, 1H), 5.55 (s, 1H), 5.28 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 166.9, 162.3, 157.5, 141.4, 140.9, 139.9, 135.2, 129, 127.6, 127.5, 127.3, 117.3, 114.3, 66.2, 51.7, 28.9. **HRMS** calcd. for $C_{24}H_{26}N_3O_2$ $[M+H]^+$: 388.2020. Found: 388.2021.



(E)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5h): According to GP D, 45 mg, 68%. **IR:** 2969.0, 1709,.0 1632.7, 1598.8, 1526.7, 1454.5, 1433.3, 1395.2, 1221.2, 1170.3, 1013.3, 856.4, 720.6, 652.7. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.41 (s, 2H), 7.51 (d, *J* = 16.0 Hz, 1H), 7.38 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 6.31 (d, *J* = 16.3 Hz, 1H), 5.57 (s, 1H), 5.19 (s, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 166.9, 162.8 (d, *J* = 247.5 Hz), 162.2, 157.5, 140, 132.1, 130.4 (d, *J* = 8 Hz), 117.2, 115.7 (d, *J* = 21.2), 114.1, 65.7, 51.6, 28.9. **^{19}F NMR** (471 MHz, CHLOROFORM-D) δ -73.69 (s). **HRMS** calcd. for $C_{18}H_{21}FN_3O_2$ $[M+H]^+$: 330.1612. Found: 330.1612.

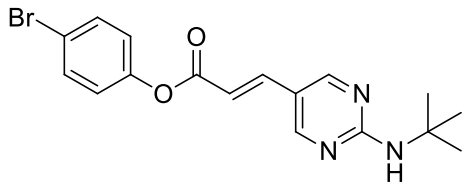


(E)-phenyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5i): According to GP D, 41 mg, 68%. **IR:** 2964.0, 1730.8, 1597.2, 1525.4, 1216.8, 1196.6, 1136.1, 1317.0, 1283.6**. ^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.48 (s, 2H), 7.66 (d, *J* = 16.1 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.16 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.47 (d, *J* = 16.1 Hz, 1H), 5.52 (s, 1H) 1.47 (s, 9H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) δ 165.5, 162.4, 157.8, 151, 141.2, 129.6, 125.9, 121.8, 117.2, 113.6, 51.7, 28.9. **HRMS** calcd. for $C_{17}H_{20}N_3O_2$ $[M+H]^+$: 298.1550. Found: 298.1551.



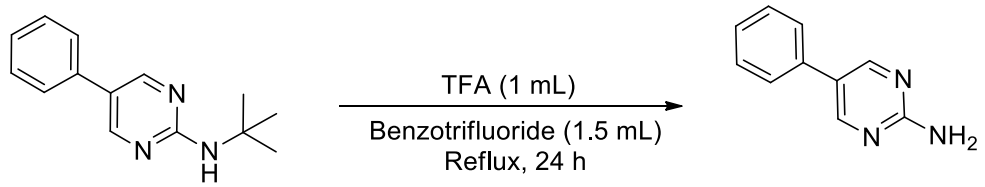
(E)-p-tolyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5j): According to GP D, 34 mg, 54%. **IR:** 2966.5, 1726.4, 1632.8, 1597.2, 1524.4, 1507.3, 1197.5, 1019.2, 962.2, 652.2. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.47 (s, 2H), 7.65 (d, *J* = 16.1 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 5.55 (s, 1H), 2.35 (s, 3H), 1.47 (s, 9H). **^{13}C NMR** (126

MHz, CHLOROFORM-D) δ 165.7, 162.4, 157.7, 148.7, 141.1, 135.5, 130.1, 121.4, 117.3, 113.7, 51.7, 28.9, 21.0. **HRMS** calcd. for $C_{18}H_{22}N_3O_2$ $[M+H]^+$: 312.1707. Found: 312.1707.



(E)-4-bromobenzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate (5k): According to GP D, 47 mg, 62%. **IR:** 2926.7, 1628.5, 1526.7, 1480.0, 1200.0, 1132.1, 1009.0, 1068.5. **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 8.48 (s, 2H), 7.66 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.44 (d, *J* = 16.1 Hz, 1H), 5.52 (s, 1H), 1.47 (s, 8H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 165.3, 162.5, 157.9, 150.0, 141.7, 132.6, 123.6, 118.9, 117.0, 113.0, 51.7, 28.9. **HRMS** calcd. For $C_{17}H_{18}BrN_3O_2$ $[M+H]^+$: 376.0655. Found: 376.0653**.**

4f: Deprotection of tert-butyl group[12]



3a, 0.2 mmol

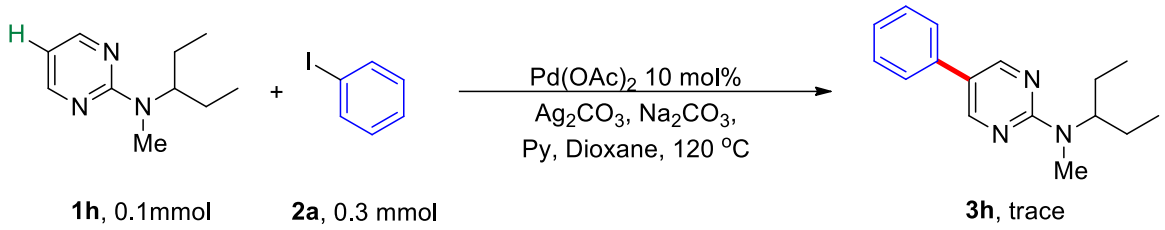
3u, 84%

An oven-dried 10 mL round bottom flask was charged with a magnetic stir-bar, **3a** (0.2 mmol) and benzotrifluoride (1.5 mL) were taken under nitrogen atmosphere. Subsequently, TFA (1.0 mL) was added. The round bottom flask was placed on a preheated oil bath at 80 °C and refluxed for 24 h. The reaction mixture was allowed to cool at room temperature and was then basified with saturated Na_2CO_3 to pH 9 and extracted with DCM. The organic layer was dried with sodium sulfate, filtered and concentrated under reduced pressure. The purification was carried out by column chromatography over silica gel (hexane/EtOAc) to give **3u** in 84% yield.

5-phenylpyrimidin-2-amine (3u)[11]: 29 mg, 84%. **^{1}H NMR** (500 MHz, CHLOROFORM-D) δ 8.53 (s, 2H), 7.48 – 7.43 (m, 4H), 7.37-7.34 (t, *J* = 7.1 Hz, 1H), 5.29 (s, 2H). **^{13}C NMR** (126 MHz, CHLOROFORM-D) 162.36, 156.63, 135.38, 129.30, 127.73, 126.19, 125.14.

4. Mechanistic Study

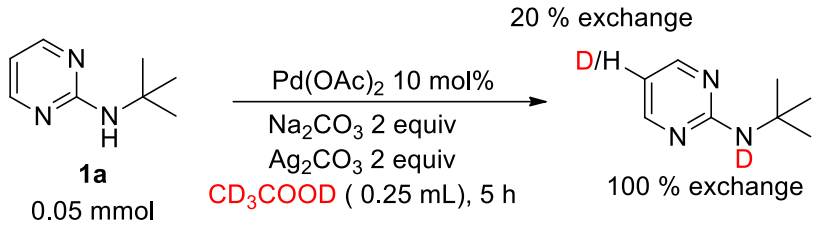
4a. Role of N-H proton in 2-aminopyrimidine



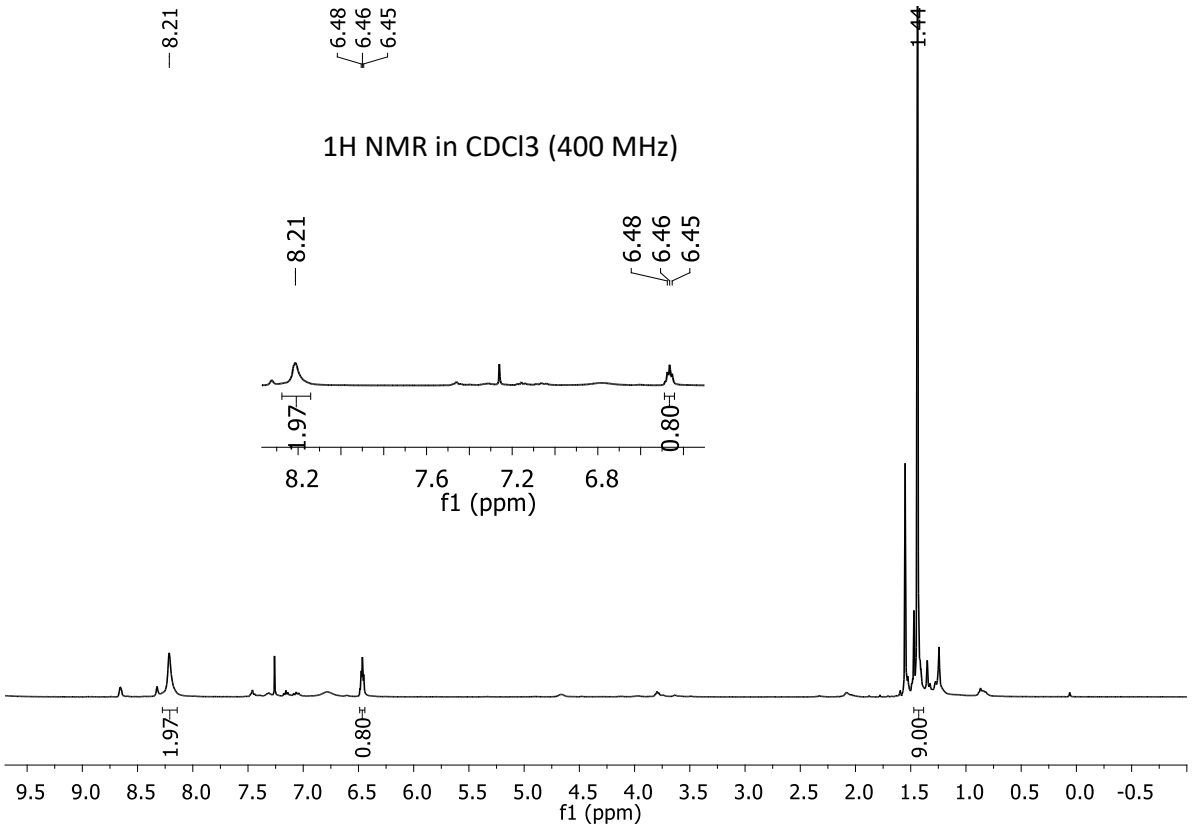
1h, 0.1mmol **2a**, 0.3 mmol **3h**, trace

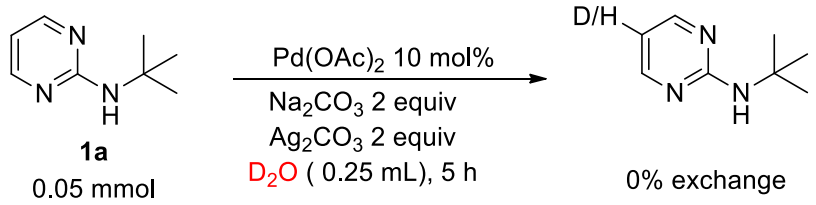
An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1h** (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (10 mol%, 0.01 mmol, 2.3 mg), Na_2CO_3 (0.2 mmol, 2 equiv, 21 mg), Ag_2CO_3 (0.2 mmol, 2 equiv, 55.2 mg) and pyridine (20 mol%, 0.02 mmol, 2 µL) were taken in air. Subsequently, Dioxane (0.5 mL) and aryl halide **2** (0.3 mmol, 3 equiv, 33 µL) were added. The reaction tube was capped tightly and placed on a preheated oil bath at 120 °C. The reaction mixture was stirred vigorously for 17 h. After that the resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The purification was carried out by column chromatography over silica gel (hexane/EtOAc) to give **3h** in trace amount. HRMS calculated for $C_{16}H_{21}N_3$ $[M+H]^+$: 255.1735. Found: 255.1726.

4b. Deuteration exchange experiment:

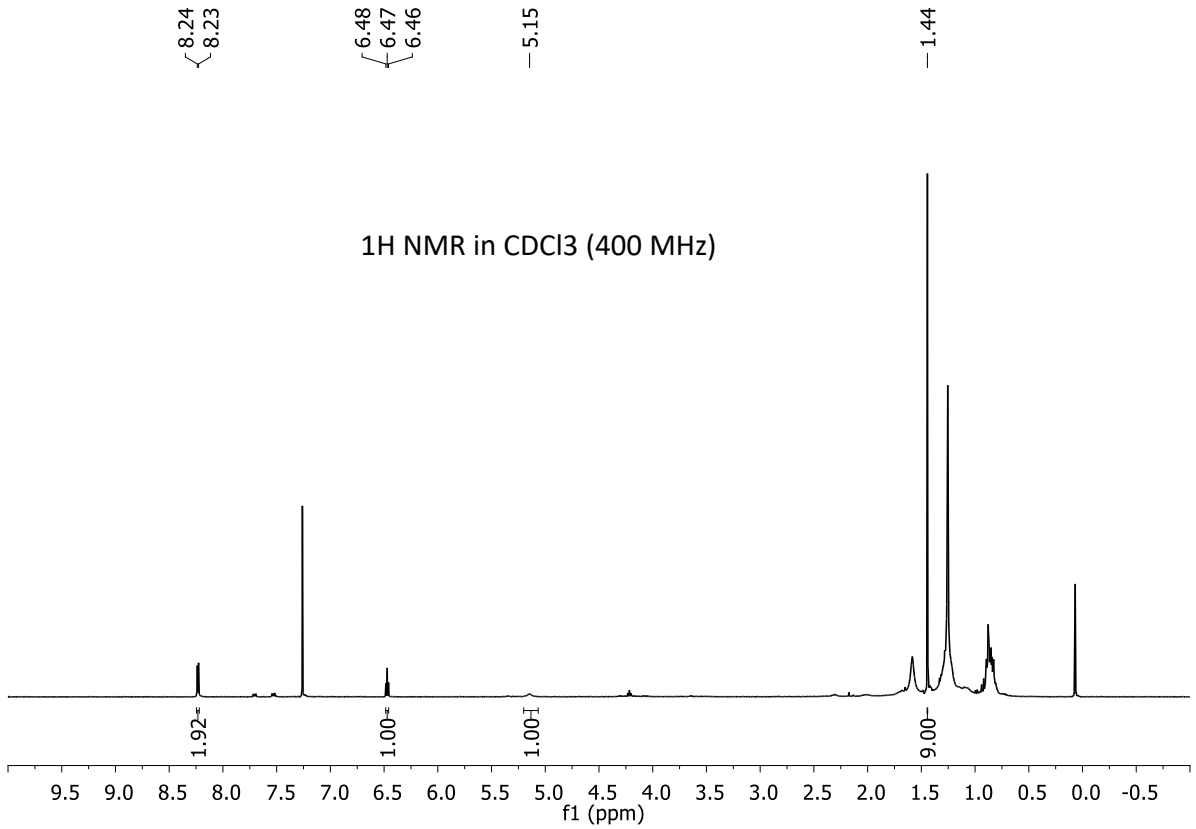


1a (0.05 mmol) was taken in a 15 mL screw cap vial and dissolved in 0.25 mL CD_3COOD. Then $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.1 mmol) and Na_2CO_3 (0.1 mmol) were added to the reaction mixture and it was allowed to stir at 120 °C for 5 h. After that the reaction mixture was neutralized with $NaHCO_3$ and extracted with ethyl acetate. Organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Then ^1H NMR of the crude sample was taken and the amount of D-exchange was measured. The D-exchange was found to be 20% at C5-position and 100% D-exchange was found at NH proton of pyrimidine.

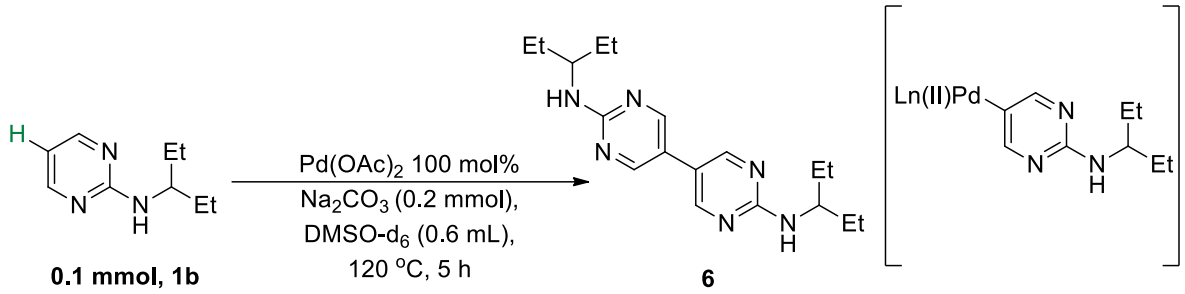




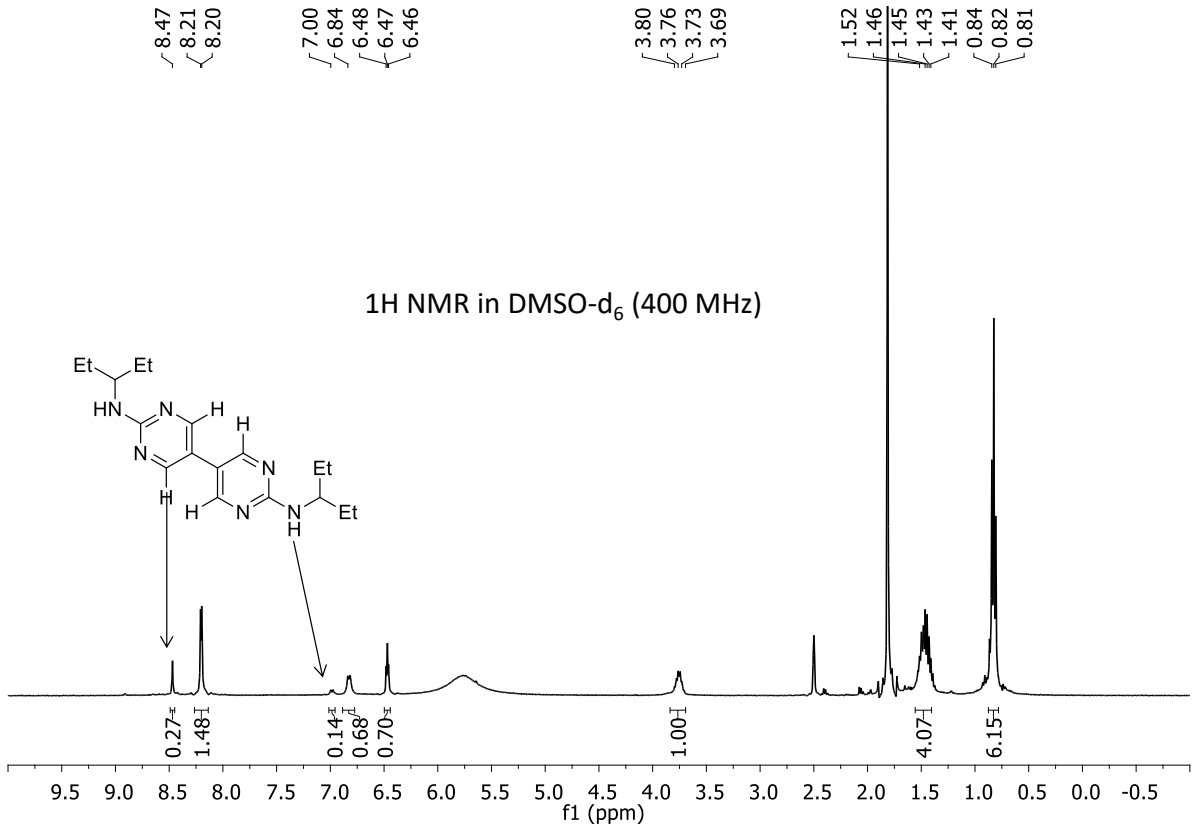
1a (0.05 mmol) was taken in a 15 mL screw cap vial and dissolved in 0.25 mL D_2O. Then $Pd(OAc)_2$ (10 mol%), Ag_2CO_3 (0.1 mmol) and Na_2CO_3 (0.1 mmol) were added to the reaction mixture and it was allowed to stir at 120 ^oC for 5 h. After that the reaction mixture was neutralized with $NaHCO_3$ and extracted with ethyl acetate. Organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Then ^1H NMR of the crude sample was taken and the amount of D-exchange was measured. No D-exchange was found at C5-position.



4c. Homocoupling reaction of 1b



In a NMR tube **1b** (0.1 mmol, 16.5 mg), $Pd(OAc)_2$ (0.1 mmol, 22.4 mg), Na_2CO_3 (0.2 mmol, 21 mg) were dissolved in DMSO-d_6 and then the NMR tube was heated at 120 °C for 5 h. The NMR tube was then brought to room temperature and ^{1}H NMR of the mixture was immediately taken. Initially we intended to trapped the C5-palladated species forming during the reaction but from ^{1}H NMR it was analysed that homocoupling of **1b** has occurred to give **6.** Later HRMS of the crude mixture was taken to confirm the formation of **6**.



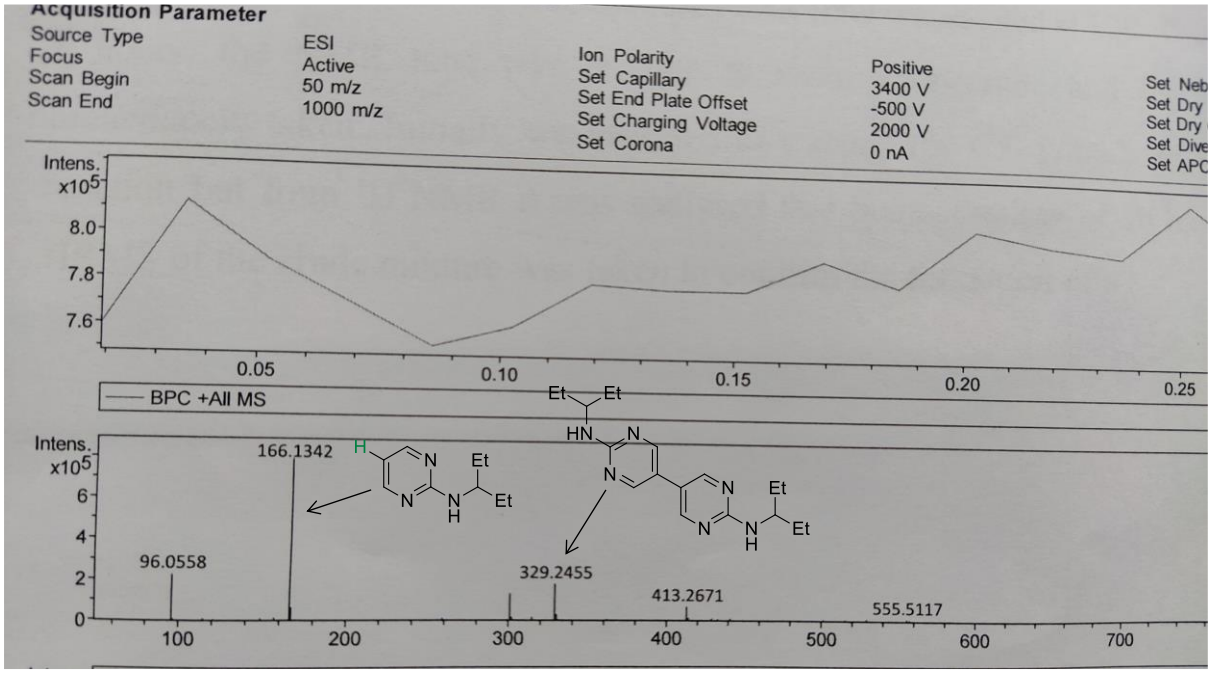
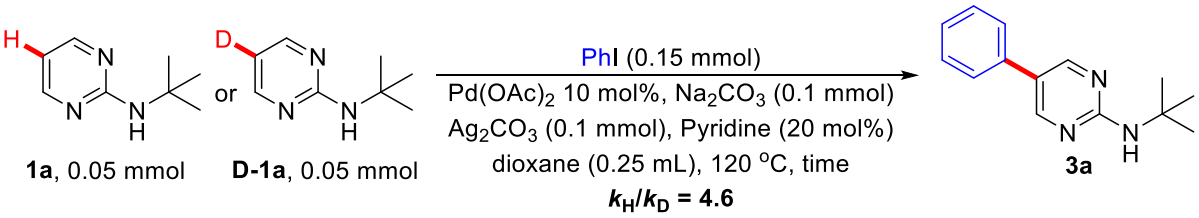


Figure S1: HRMS data

4d. Kinetic isotope Experiments:



To two oven dried 15 mL sealed tubes were added $Pd(OAc)_2$ (10 mol%), Na_2CO_3 (0.1 mmol), Ag_2CO_3 (0.1 mmol) and 1,2,4,5-tetramethylbenzene (0.05 mmol, 6.7 mg) as internal standard. In one tube, dioxane (0.25 mL), **1a** (0.05 mmol), iodobenzene (3 equiv) and pyridine (20 mol%) were added subsequently. In the other tube, dioxane (0.25 mL), **D-1a** (0.05 mmol), iodobenzene (3 equiv) and pyridine (20 mol%) were added. Then the reactions were stirred at 120 °C and yield of **3a** was determined by GC using 1,2,4,5-tetramethylbenzene as internal standard. The yield (%) vs time (h) plot was found to be linear plot and from the slop of such plot the KIE value k_H/k_D = 4.6 was determined.

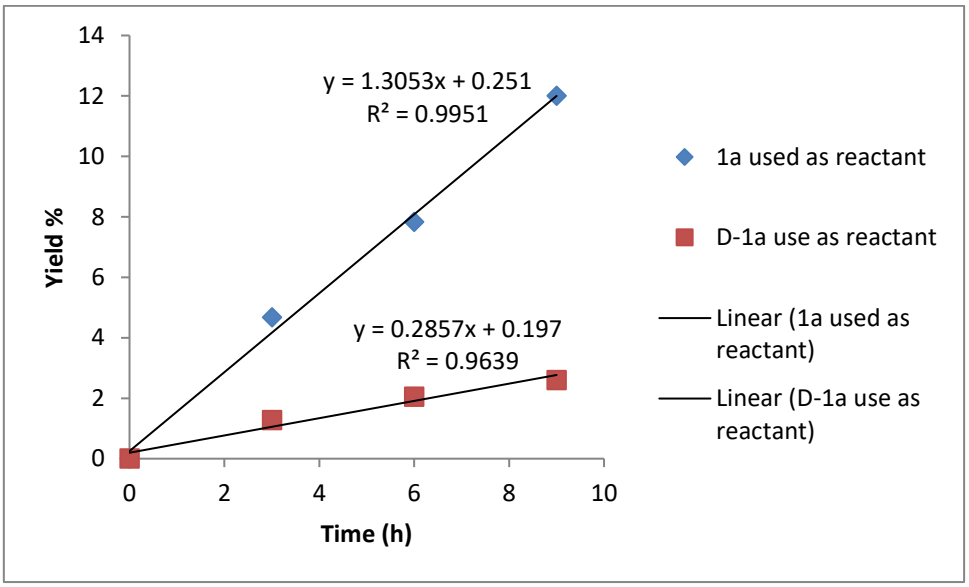
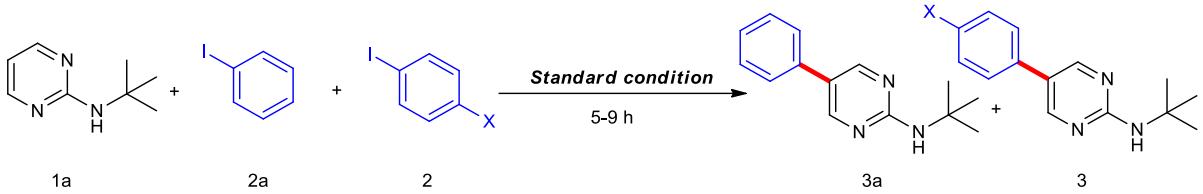


Figure S2: KIE Measurement by GC analysis

4e. Hammett analysis



In three different 15 mL screw cap vials, **1a** (15 mg, 0.1 mmol) and iodobenzene (17 µL, 0.15 mmol) were dissolved in 0.5 mL 1,4-dioxane. Next $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), Na_2CO_3 (21 mg, 0.2 mmol), Ag_2CO_3 (55 mg, 0.2 mmol), pyridine (2 µL, 0.02 mmol) and iodobenzene derivatives **2b, 2e, 2g** (0.15 mmol) were added to the three different vials, respectively. The vials containing the reaction mixture were heated at 120 °C and at three different intervals of time (5 hr, 7 hr and 9 hr) the yields of the products were measured using GC by taking out 10 µL of the reaction mixture from the respective vials, passed through a bed of celite and diluted with ethyl acetate. The ratios of yields (**3a:3h**), (**3a:3j**) and (**3a: 3m**) were estimated by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard. The measured average value of the slope was found to be 1.67.

Time	Conversion of (**1a**)	GC Yield
5 hr	34%	**3a** (22%), **3h** (11%)
	35%	**3a** (25%), **3j** (7%)
	36%	**3a** 10.4%, **3m** (21%)
7 hr	42%	**3a** (28.8%), **3h** (14.8%)
	40%	**3a** (29%), **3j** (8.5%)
	50%	**3a** (14.9%), **3m** (32.8)
9 hr	63%	**3a** (36%), **3h** (19%)
	65%	**3a** (38%), **3j** (12.8%)
	60%	**3a** (18%), **3m** (38%)

X	**σ**	log (k_X/k_H) (5 hr)	log (k_X/k_H) (6 hr)	log (k_X/k_H) (7 hr)	log (k_X/k_H) (9 hr)	log $(k_X/k_H)_{average}$	Standard deviation
p-OMe	-0.27	-0.55	-0.52	-0.53	-0.48	-0.52	0.029
p-Me	-0.17	-0.3	-0.30	-0.29	-0.27	-0.29	0.014
H	0	0	0	0	0	0	0
P-Cl	0.23	0.31	0.36	0.35	0.32	0.33	0.024

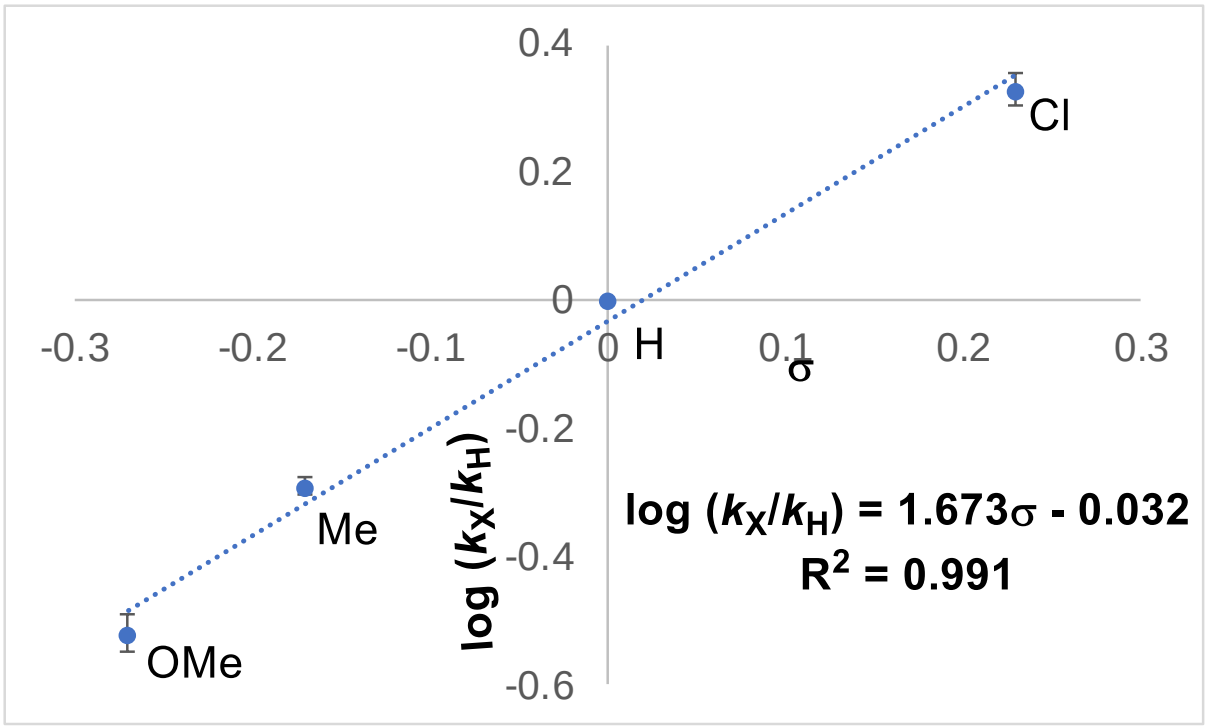
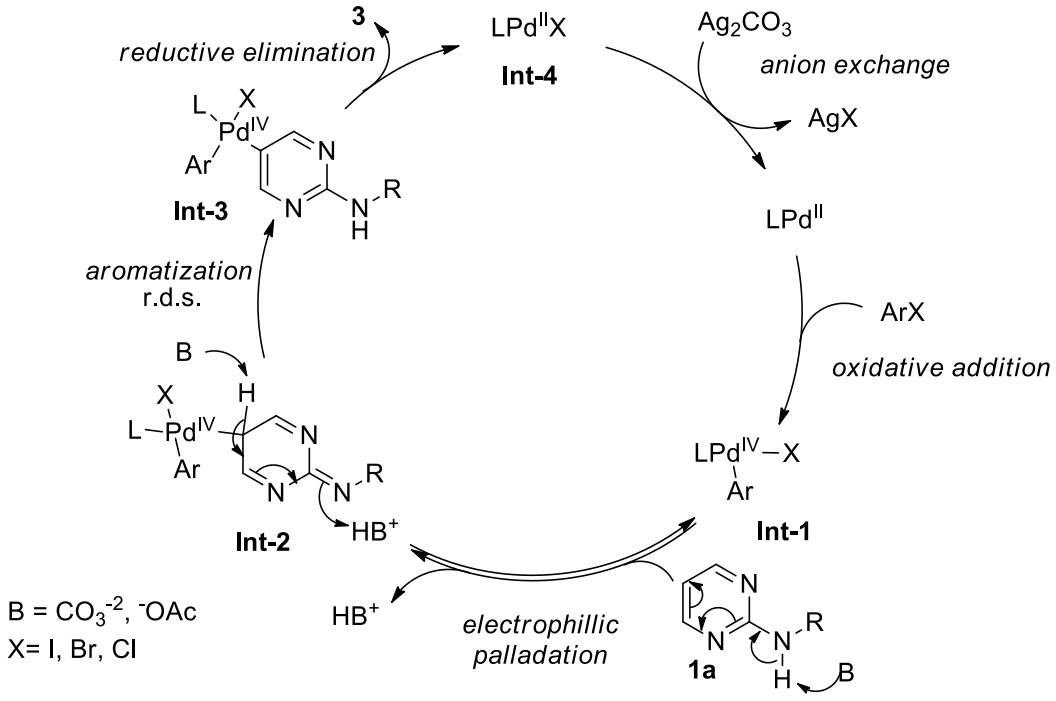


Figure S3: Hammett Plot

4g. Mechanism

Mechanism of Arylation

In the presence of aryl halide, Pd(II) species underwent oxidative addition to form Pd(IV) intermediate **Int-1**. Then the base mediated deprotonation and delocalisation of electron density afforded the electrophilic palladation step **Int-2**. Rearomatization at the rate-determining step gave the corresponding C5-palladated species **Int-3**, which undergo subsequent the reductive elimination to provide the desired arylated product **3**. Finally, ligand dissociation from **Int-4** and halide abstraction by silver carbonate regenerated the active Pd(II)-species for the next cycle.



Mechanism of olefination

We suggested a detailed catalytic cycle of the dehydrogenative olefination reaction (Figure S3). The key intermediates are as follows: (1) At first base mediated deprotonation of **1a** formed the palladated species **A.** (2) The alkene **4** underwent coordination with **A** to form intermediate **B** and further migratory insertion led to the formation of intermediate **C**. (3) *β*-Hydride *syn*-elimination afforded the the final product **5** along with the generation of palladium hydride intermediate **D**. (4) The reductive elimination releases HOAc to form Pd(0), which is then reoxidized by Cu-salt to regenerate the Pd(II) catalyst.

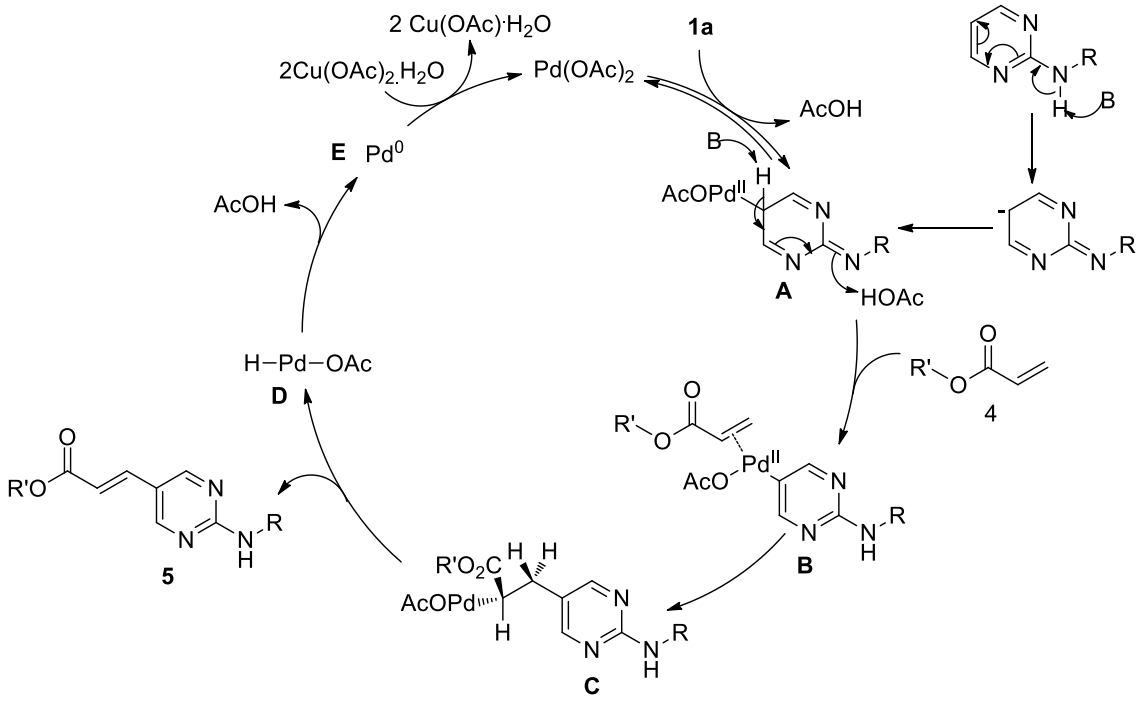
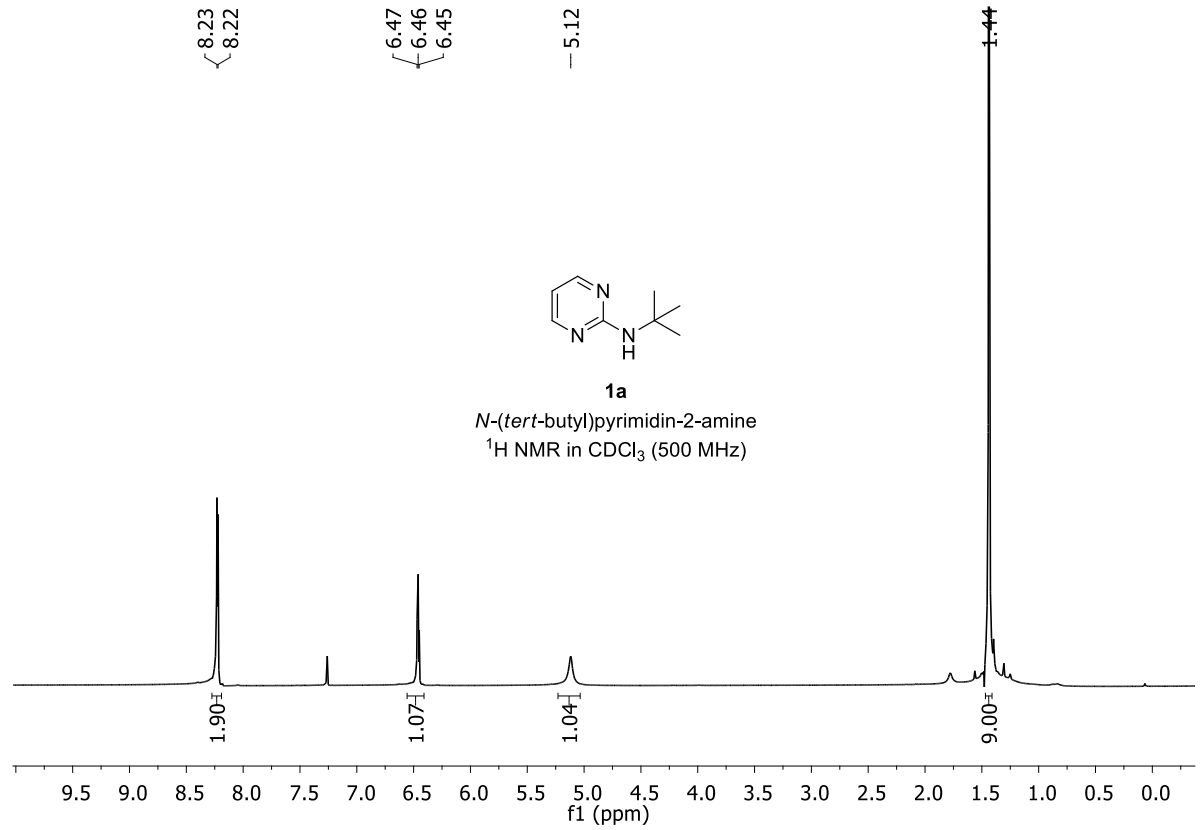


Figure S4: Detailed mechanism of the dehydrogenative olefination of the 2-aminopyrimidine **1a**.

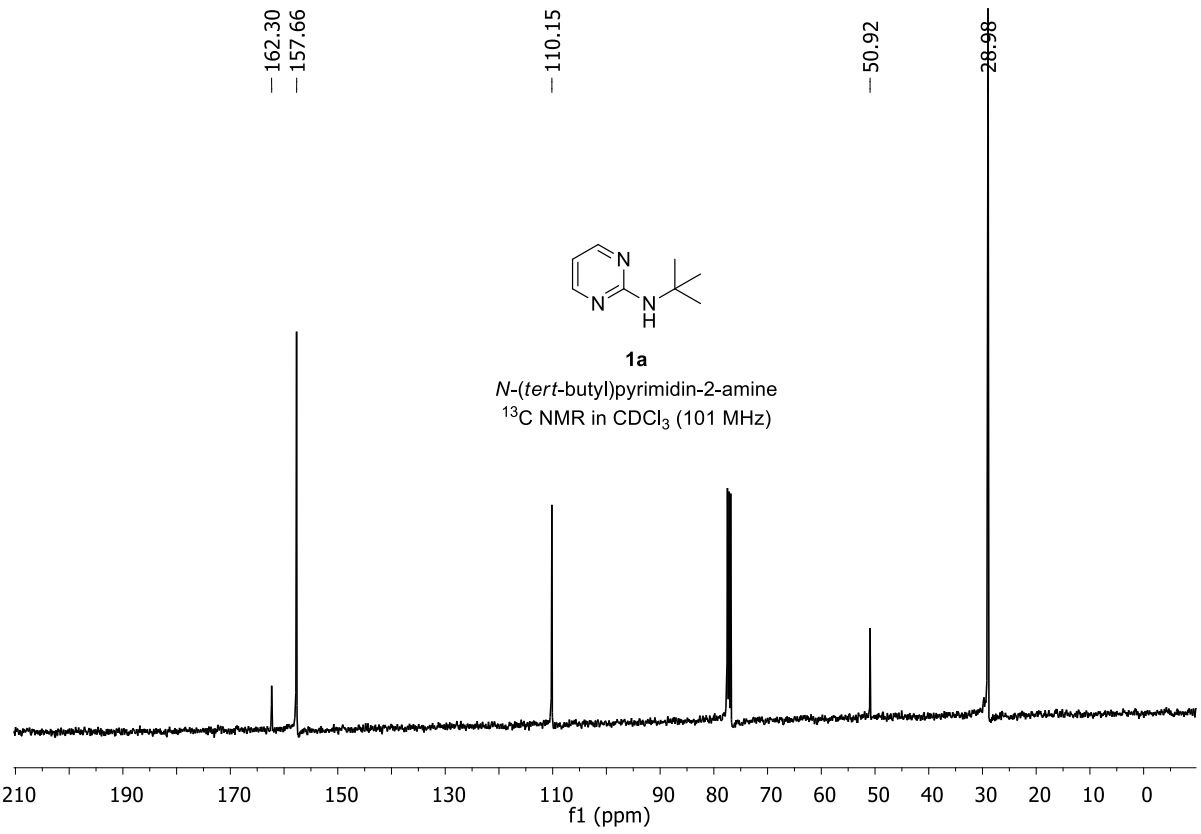
5. Copies of NMR Spectra



1a

N-(*tert*-butyl)pyrimidin-2-amine

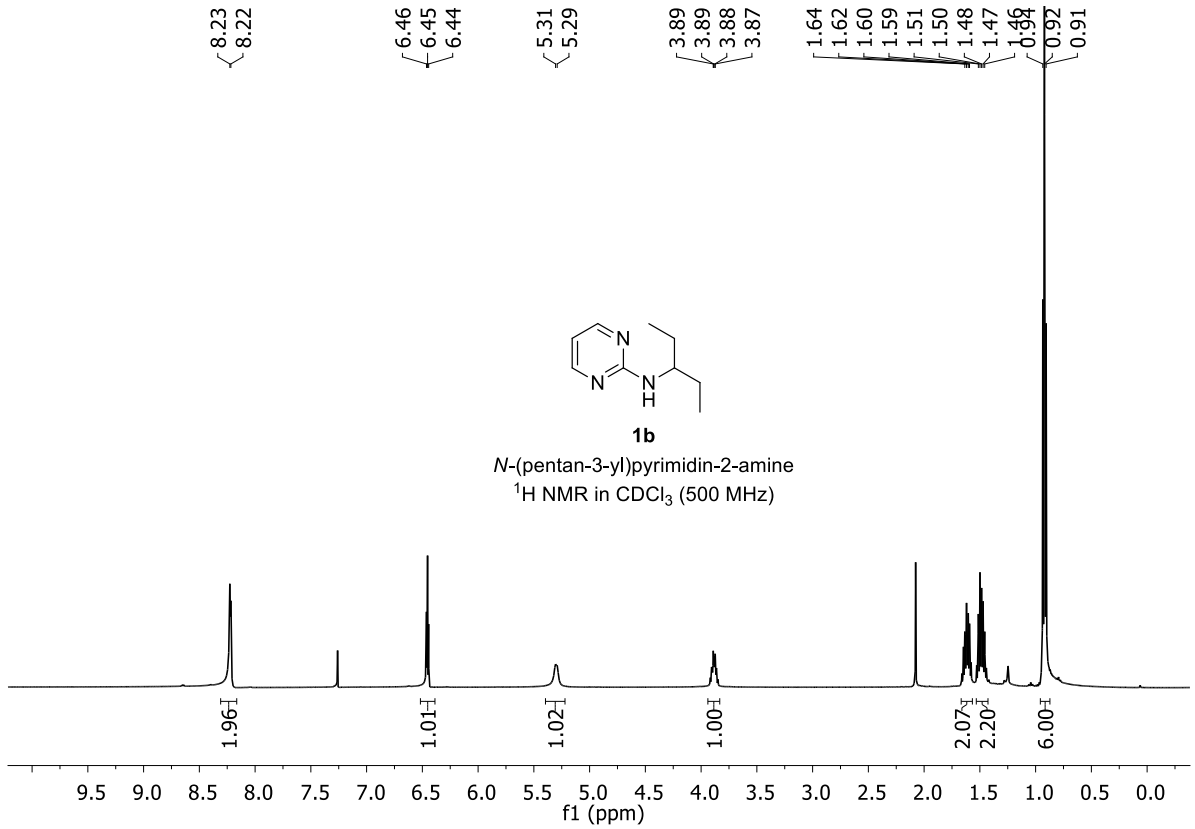
^{1}H NMR in $CDCl_3$ (500 MHz)



1a

N-(*tert*-butyl)pyrimidin-2-amine

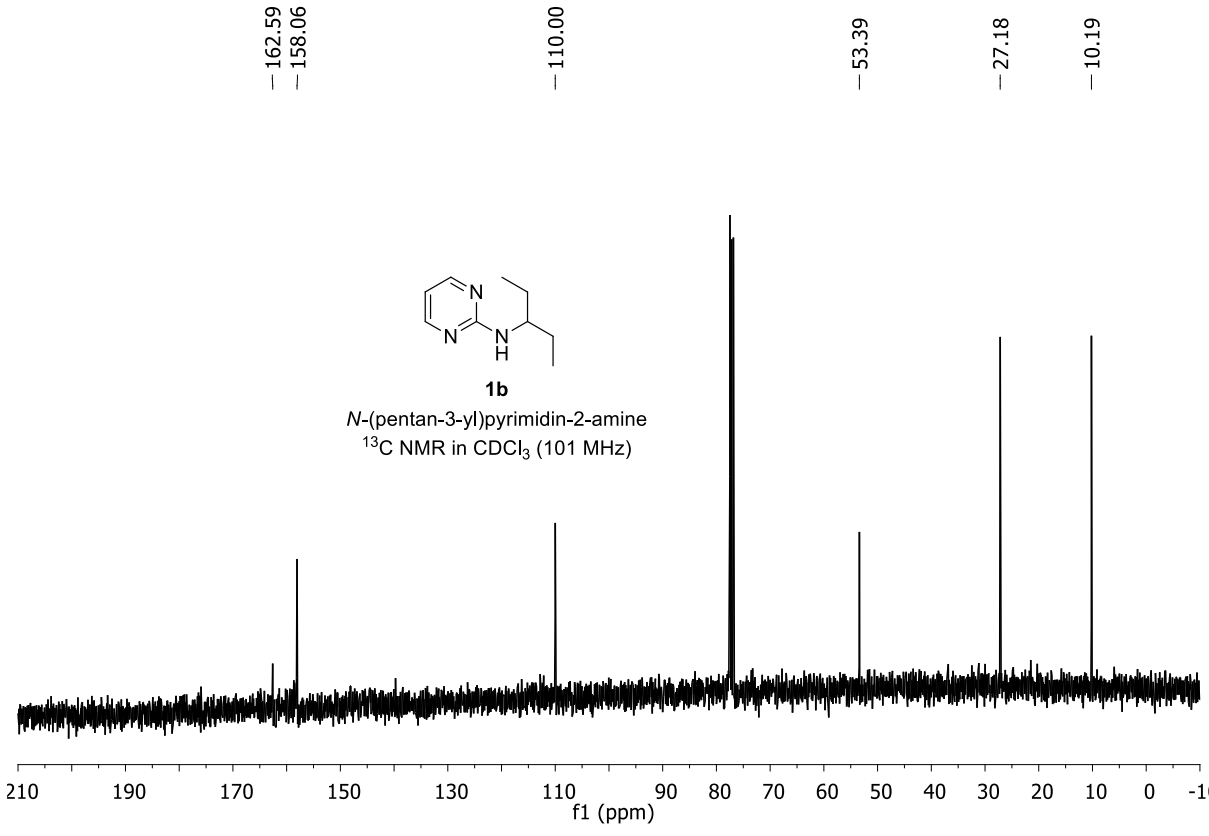
^{13}C NMR in $CDCl_3$ (101 MHz)



1b

N-(pentan-3-yl)pyrimidin-2-amine

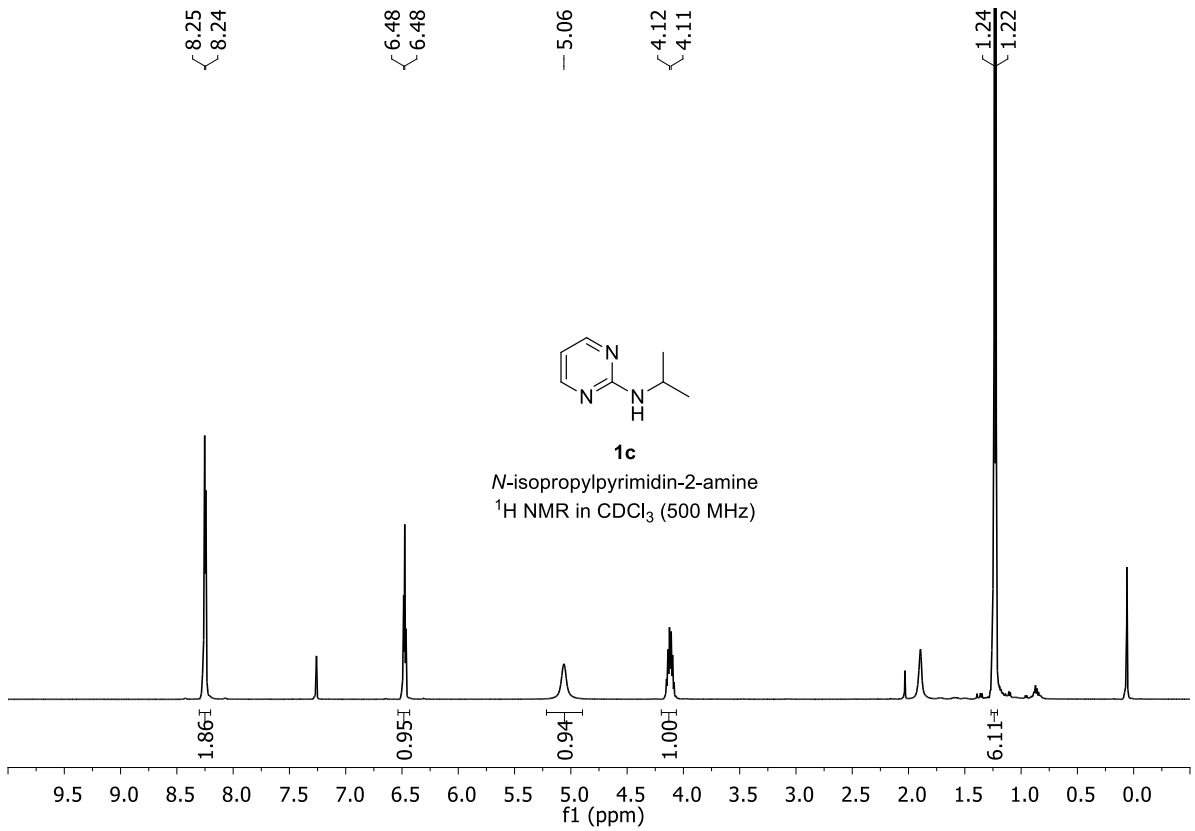
^{1}H NMR in $CDCl_3$ (500 MHz)

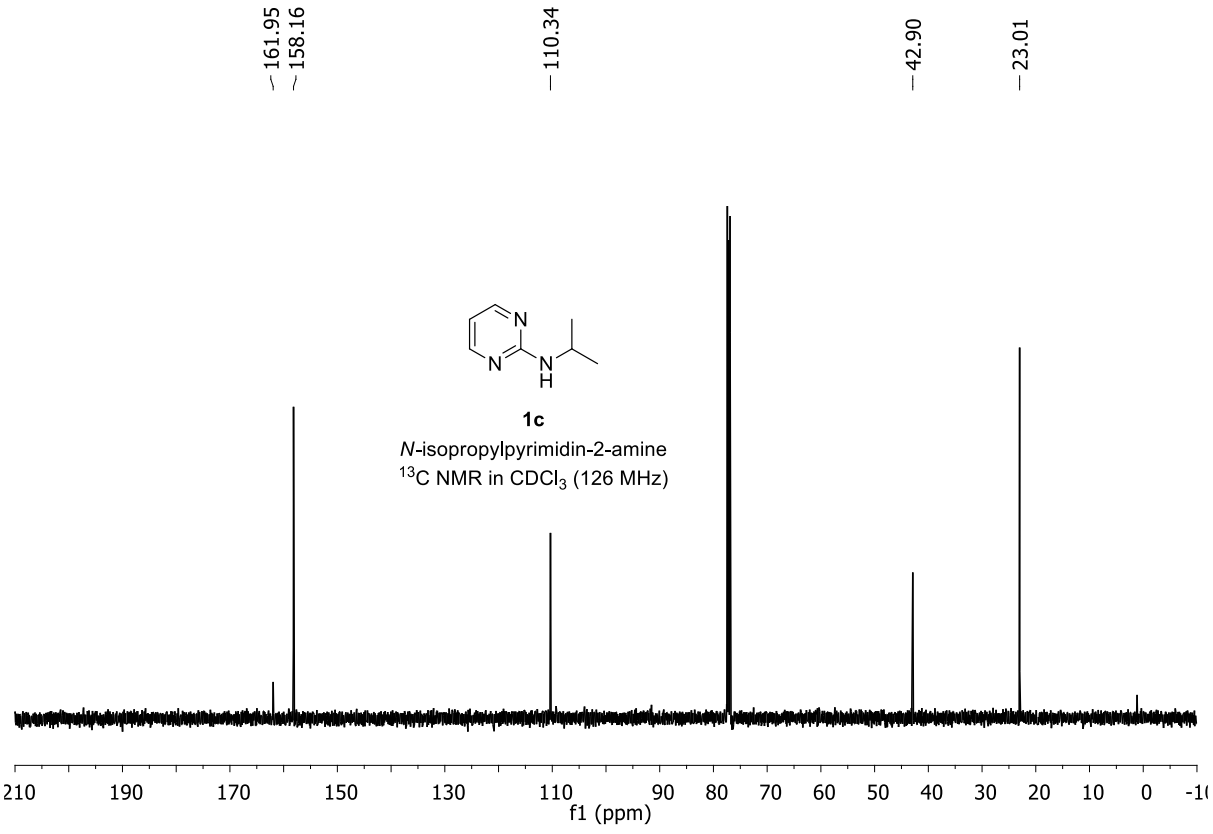


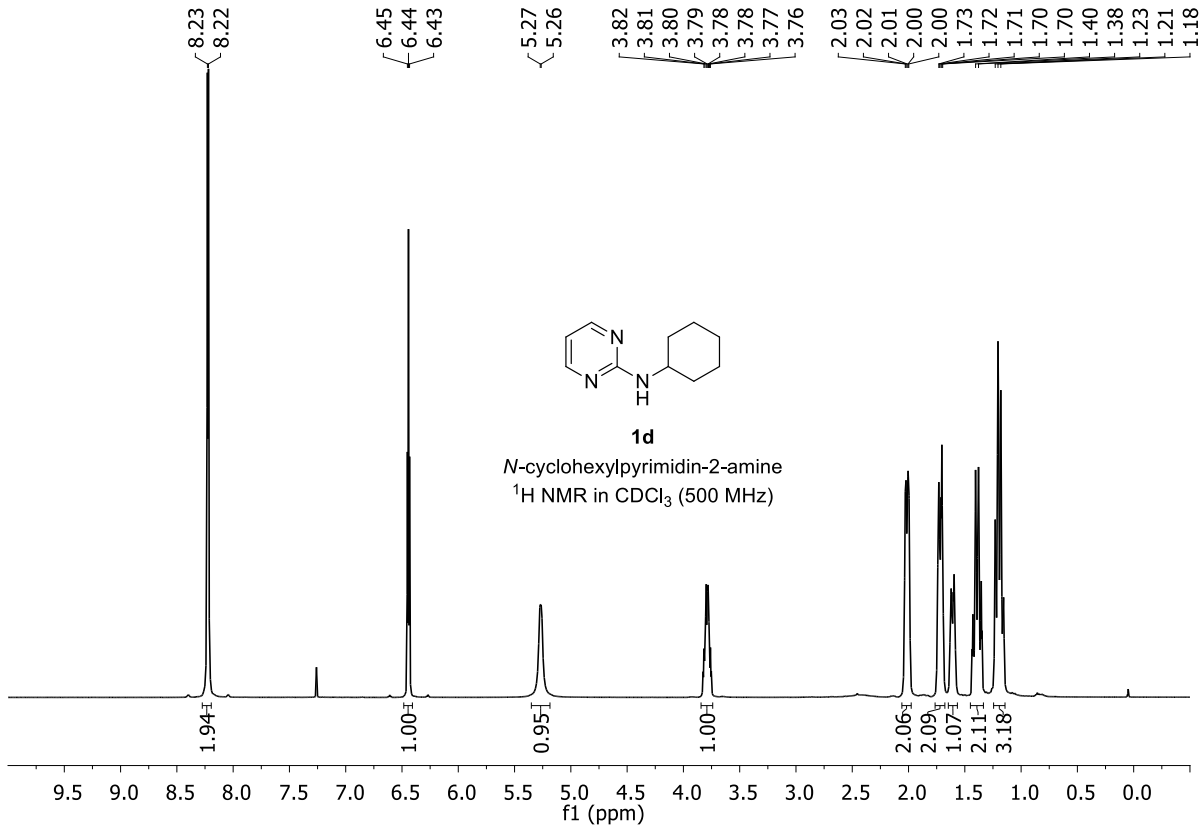
1b

N-(pentan-3-yl)pyrimidin-2-amine

^{13}C NMR in $CDCl_3$ (101 MHz)


8.25
8.24
6.48
6.48
5.06
4.12
4.11
1.24
1.22
1.86
0.95
0.94
1.00
6.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1c
N-isopropylpyrimidin-2-amine
1H NMR in CDCl3 (500 MHz)


161.95
158.16
110.34
42.90
23.01
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1c
N-isopropylpyrimidin-2-amine
13C NMR in CDCl3 (126 MHz)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3.80
3.79
3.78
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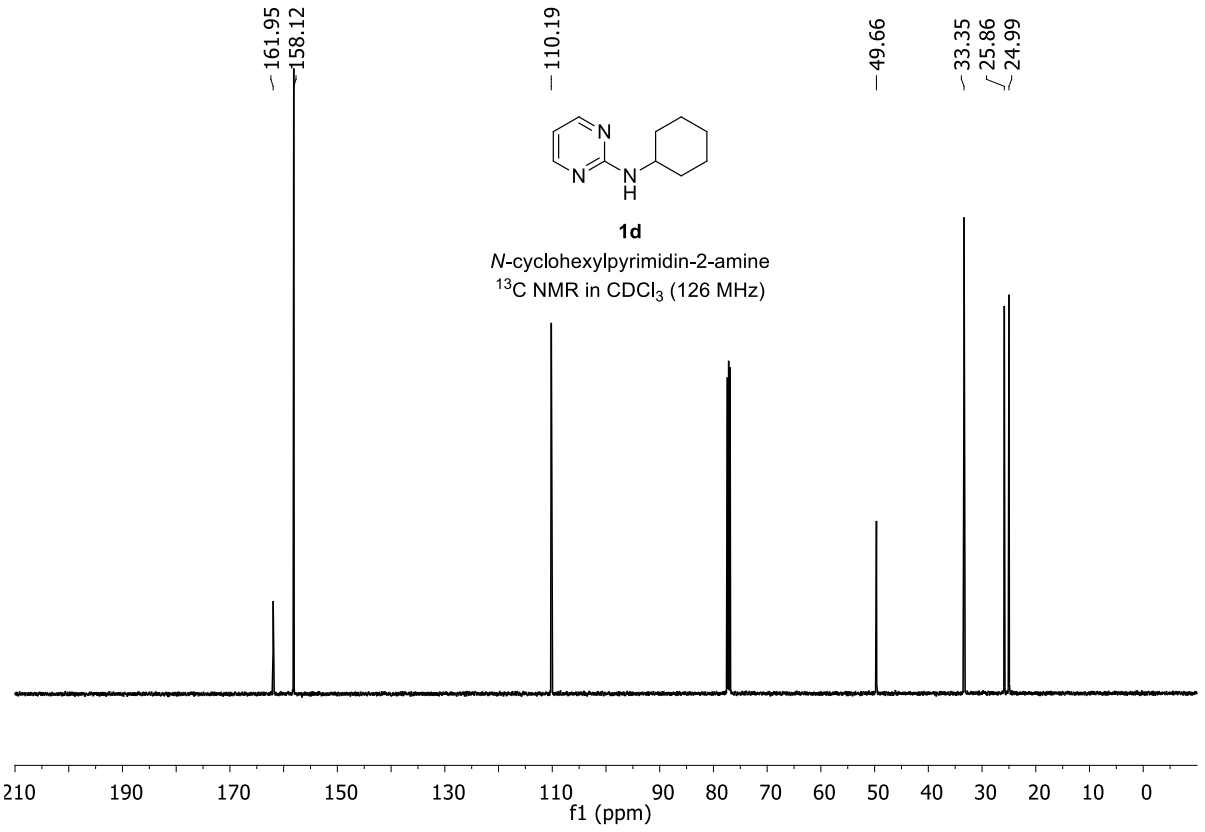
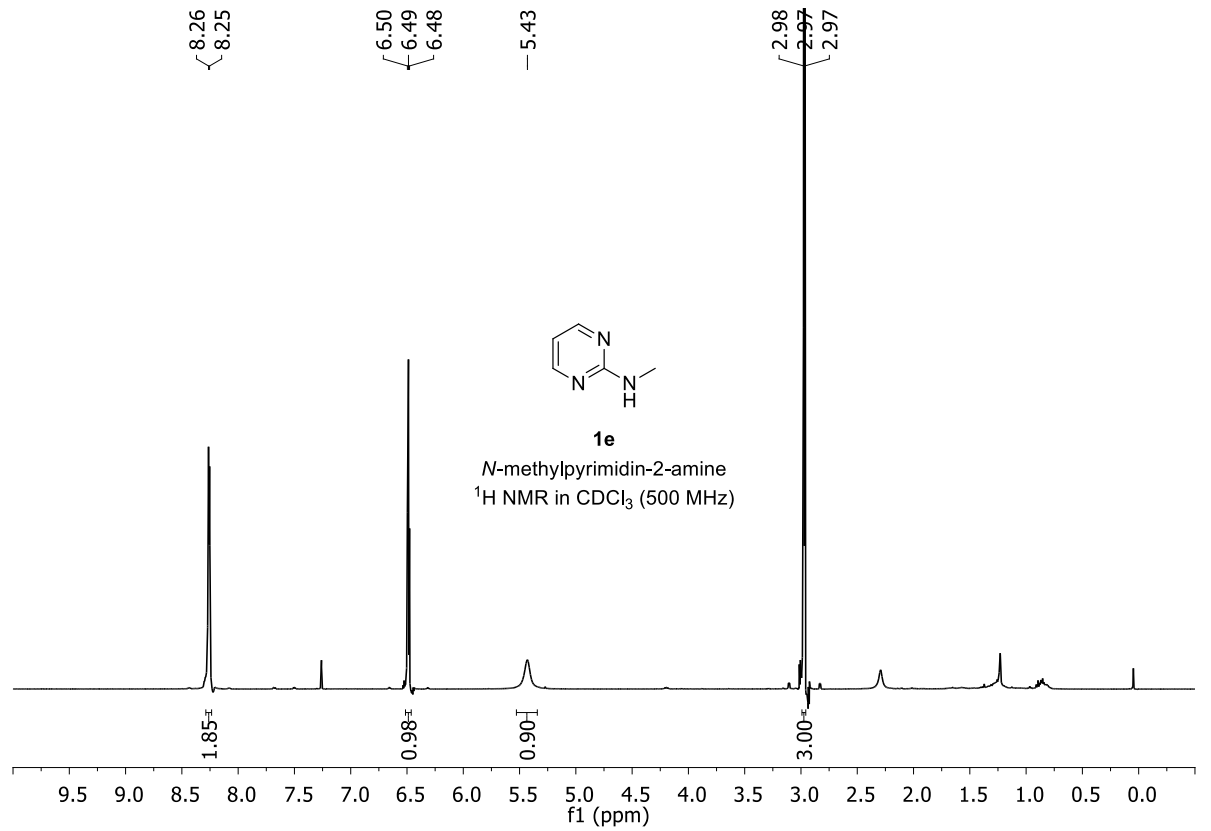
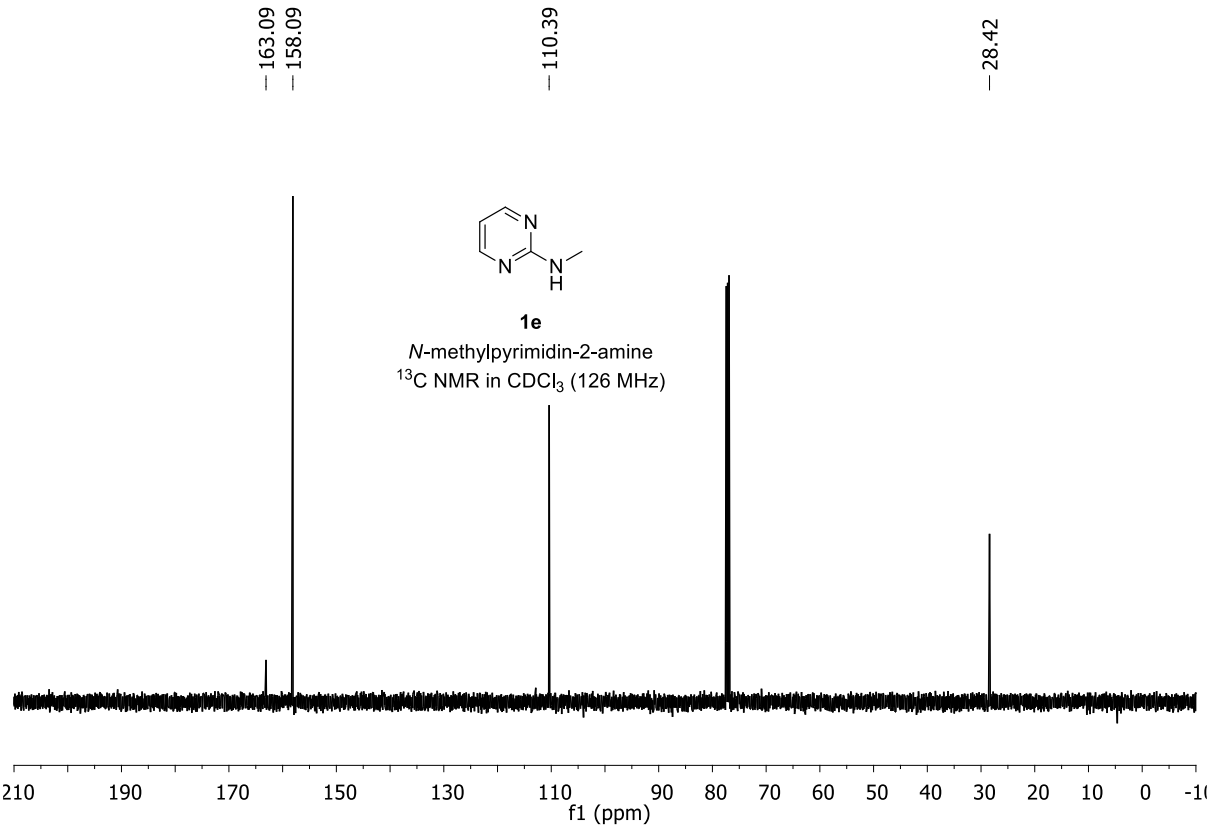
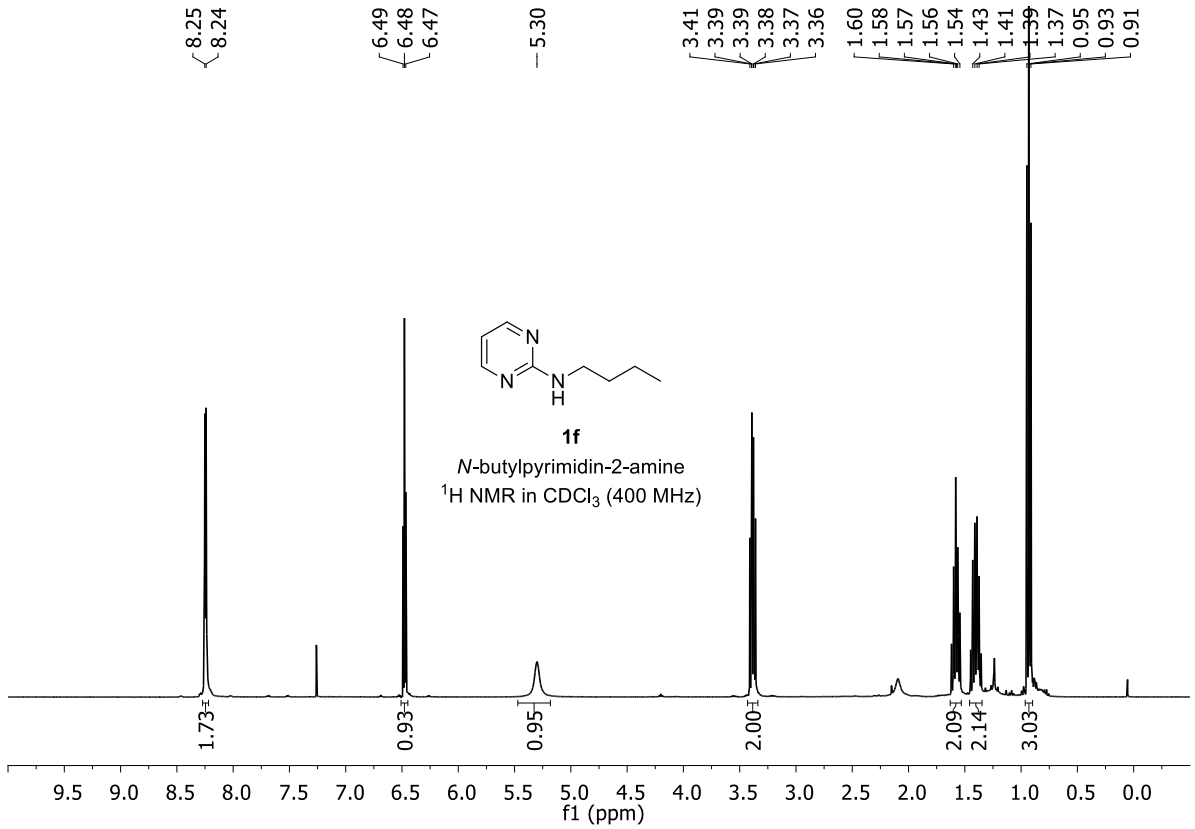
3.76
2.03
2.02
2.01
2.00
2.00
1.73
1.72
1.71
1.70
1.70
1.40
1.38
1.23
1.21
1.18
1d
N-cyclohexylpyrimidin-2-amine
1H NMR in CDCl3 (500 MHz)
1.94
1.00
0.95
1.00
2.06
2.09
1.07
2.11
3.18
f1 (ppm)


161.95
158.12
110.19
49.66
33.35
25.86
24.99
1d
N-cyclohexylpyrimidin-2-amine
13C NMR in CDCl3 (126 MHz)
f1 (ppm)


8.26
8.25
6.50
6.49
6.48
5.43
2.98
2.97
2.97
1.85
0.98
0.90
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
1e
N-methylpyrimidin-2-amine
1H NMR in CDCl3 (500 MHz)

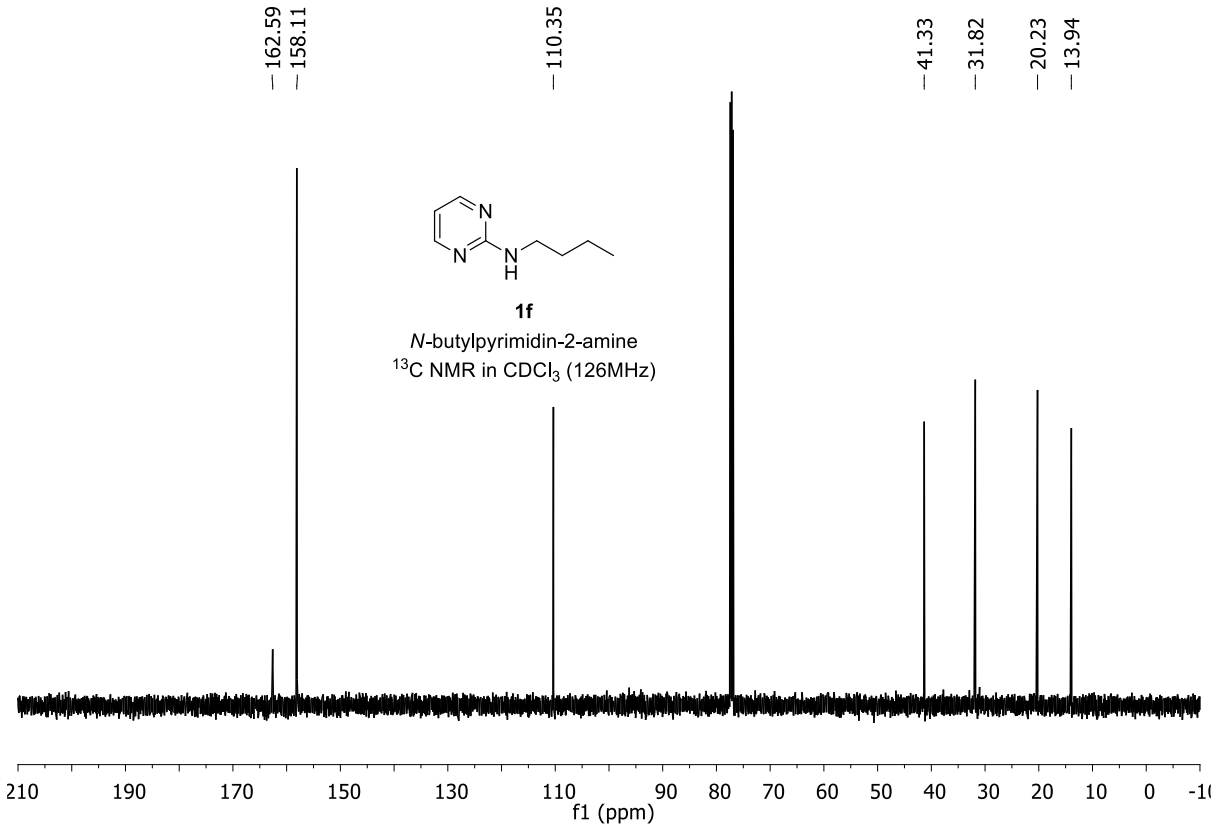

163.09
158.09
110.39
28.42
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1e
N-methylpyrimidin-2-amine
13C NMR in CDCl3 (126 MHz)



1f

N-butylpyrimidin-2-amine

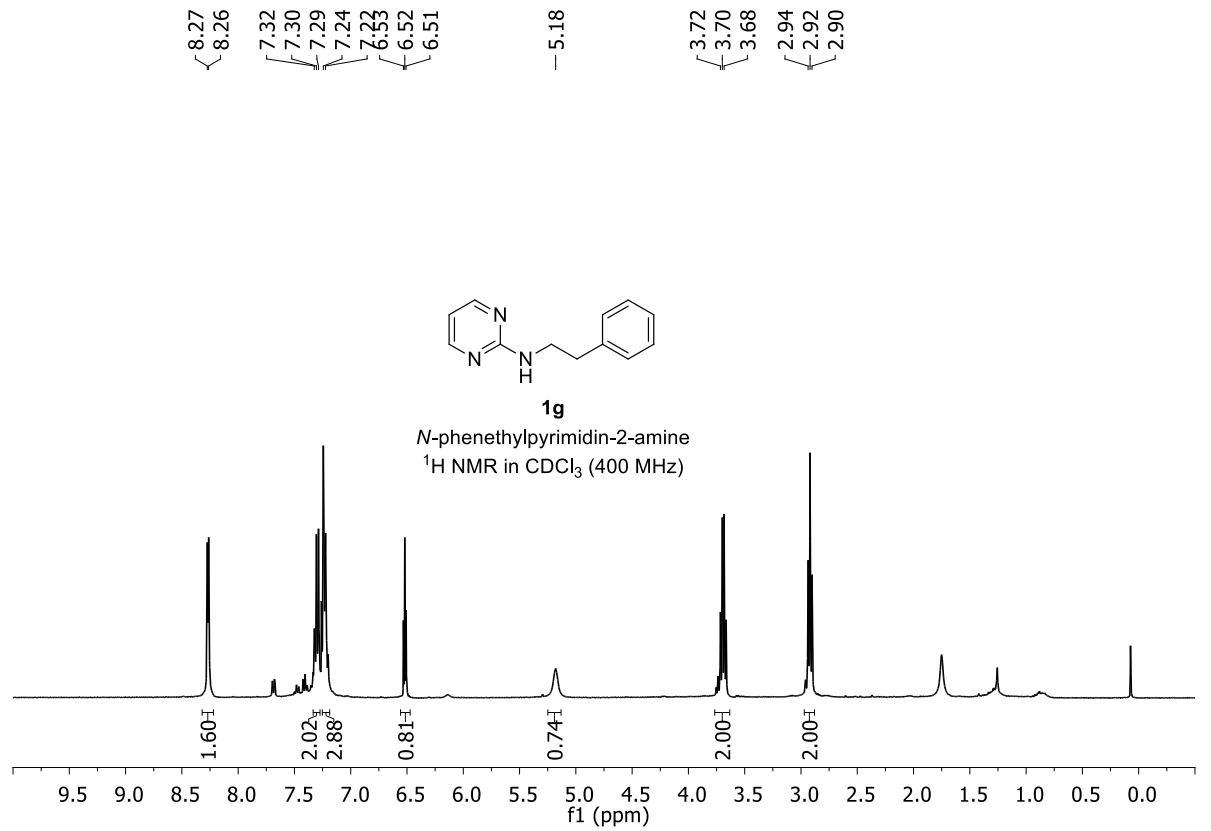
^{1}H NMR in $CDCl_3$ (400 MHz)

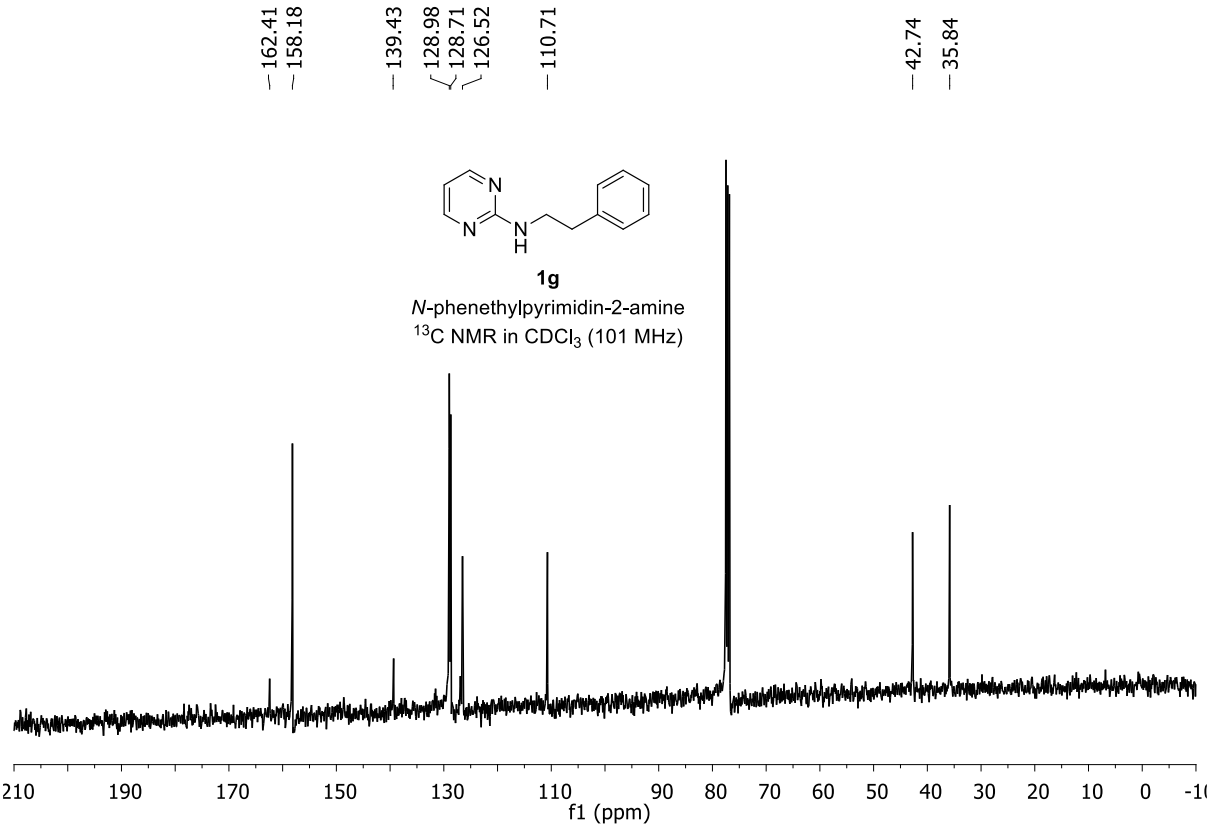


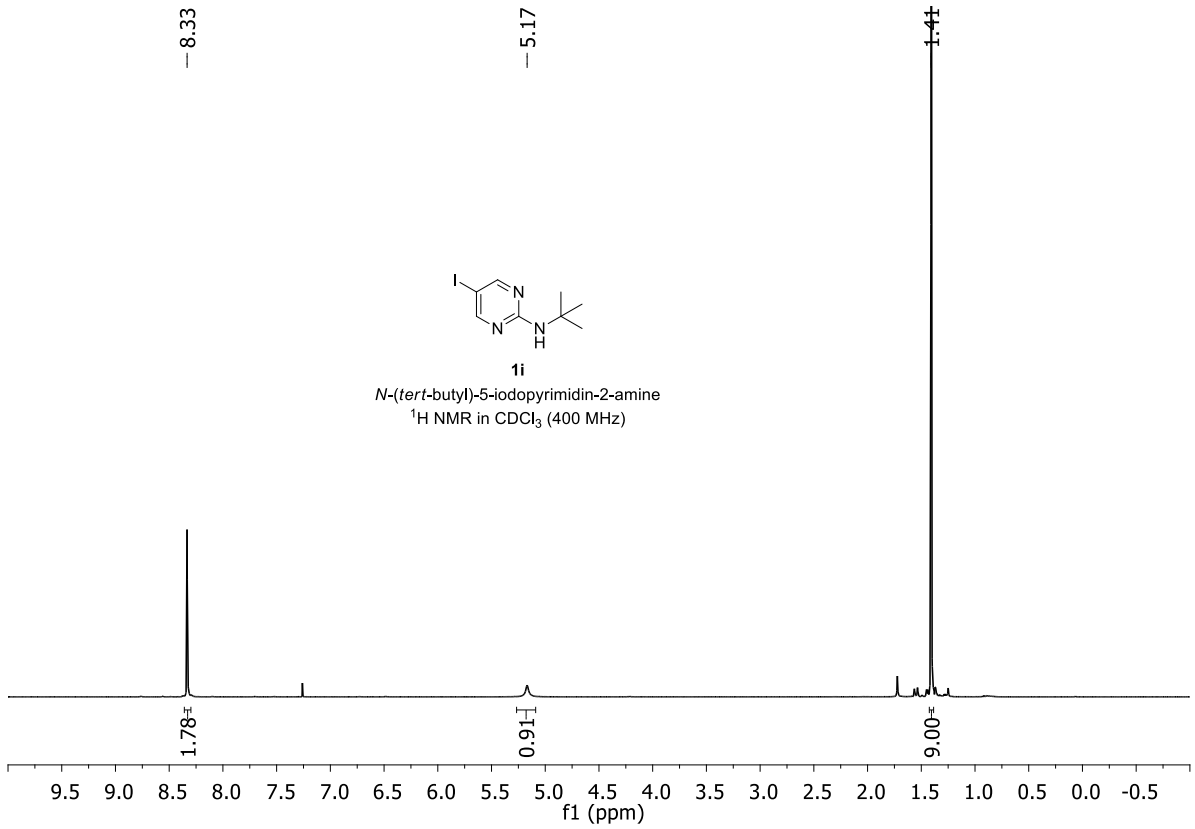
1f

N-butylpyrimidin-2-amine

^{13}C NMR in $CDCl_3$ (126MHz)


8.27
8.26
7.32
7.30
7.29
7.24
7.22
6.53
6.52
6.51
5.18
3.72
3.70
3.68
2.94
2.92
2.90
1g
N-phenethylpyrimidin-2-amine
1H NMR in CDCl3 (400 MHz)
1.60
2.02
2.88
0.81
0.74
2.00
2.00
f1 (ppm)

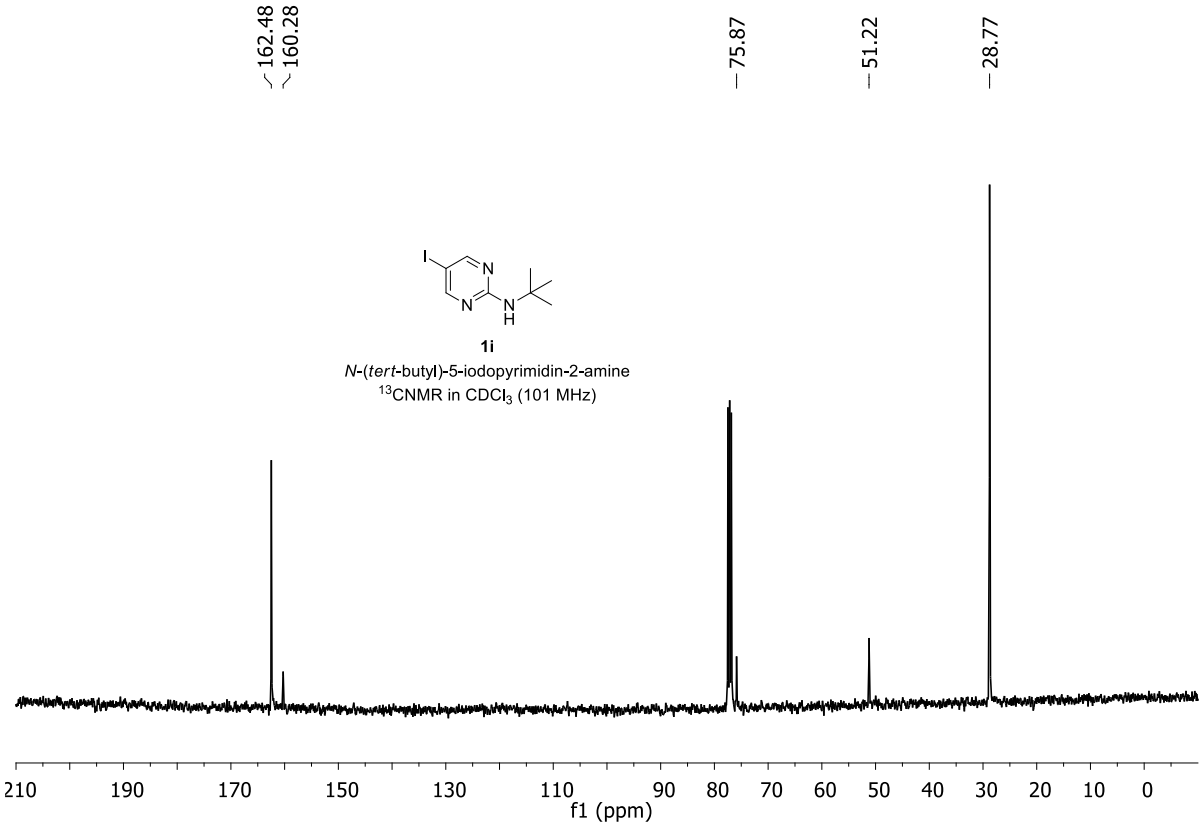

162.41
158.18
139.43
128.98
128.71
126.52
110.71
42.74
35.84
1g
N-phenethylpyrimidin-2-amine
13C NMR in CDCl3 (101 MHz)
f1 (ppm)



1i

N-(*tert*-butyl)-5-iodopyrimidin-2-amine

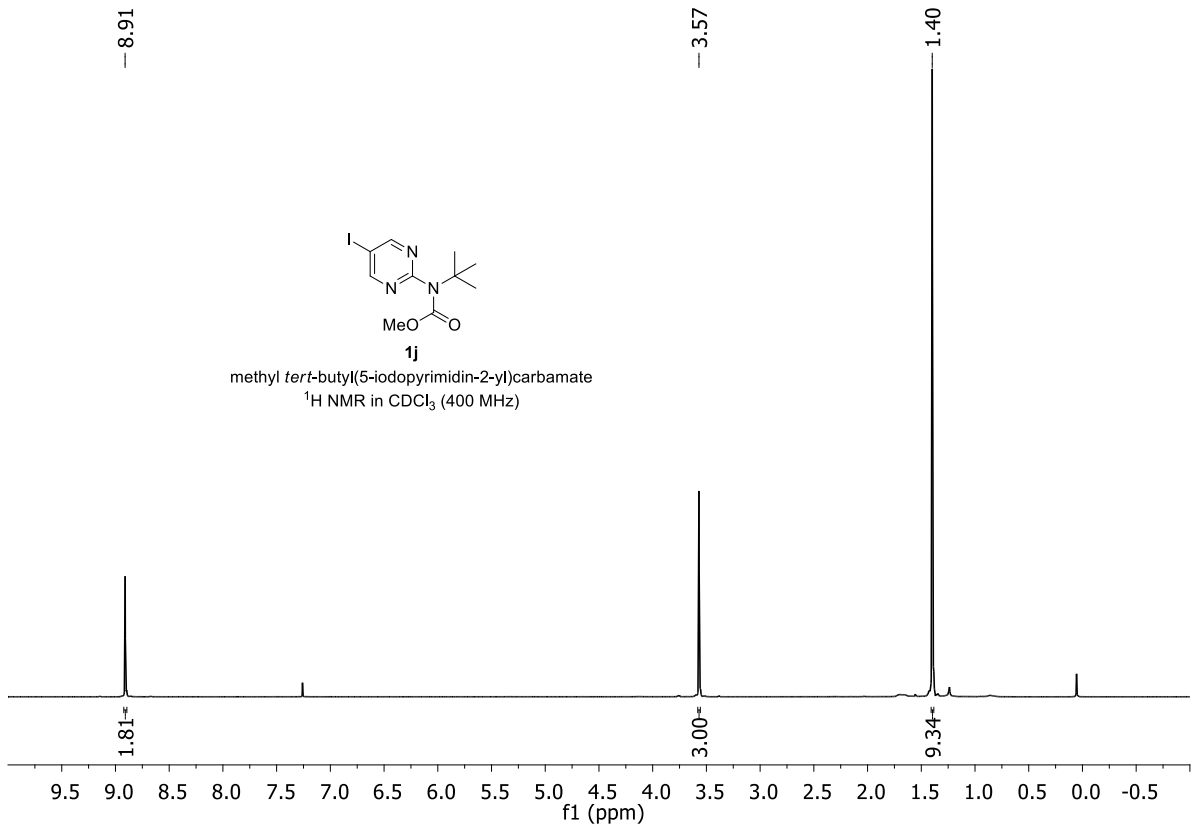
^{1}H NMR in $CDCl_3$ (400 MHz)

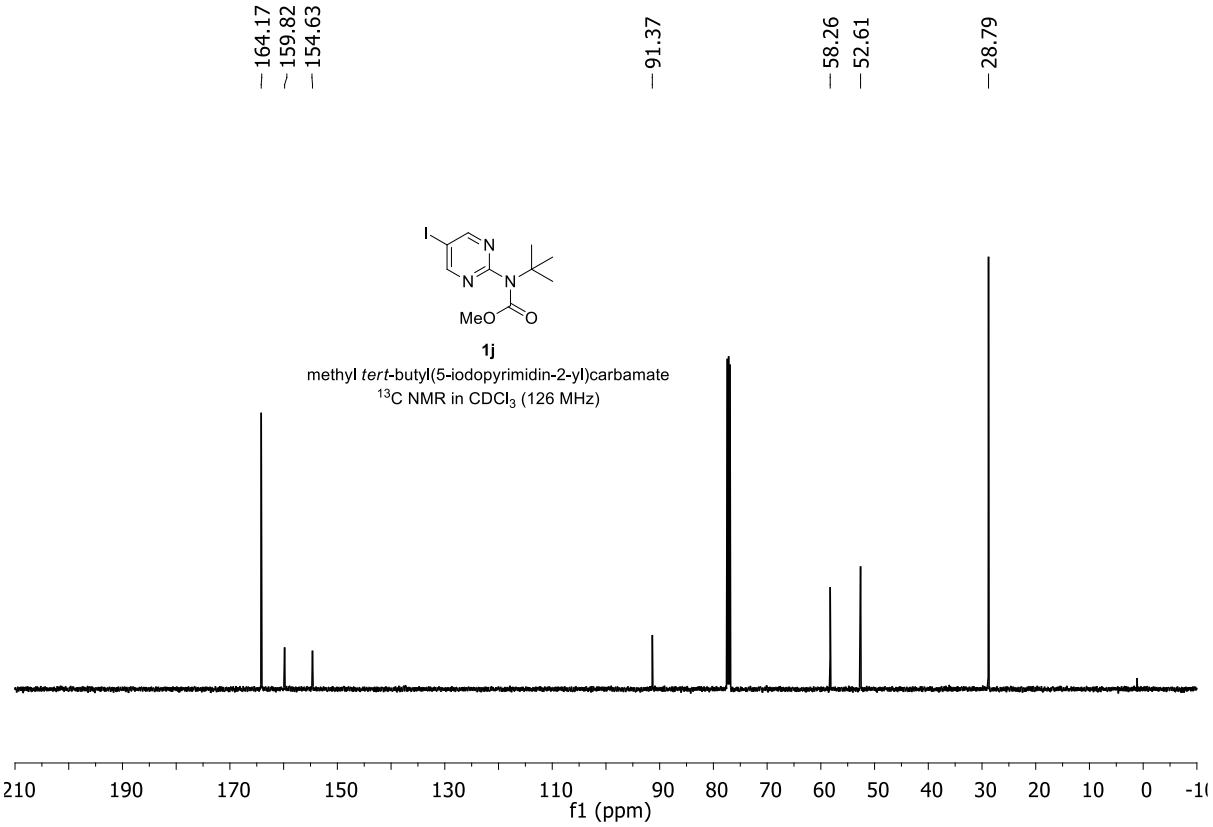


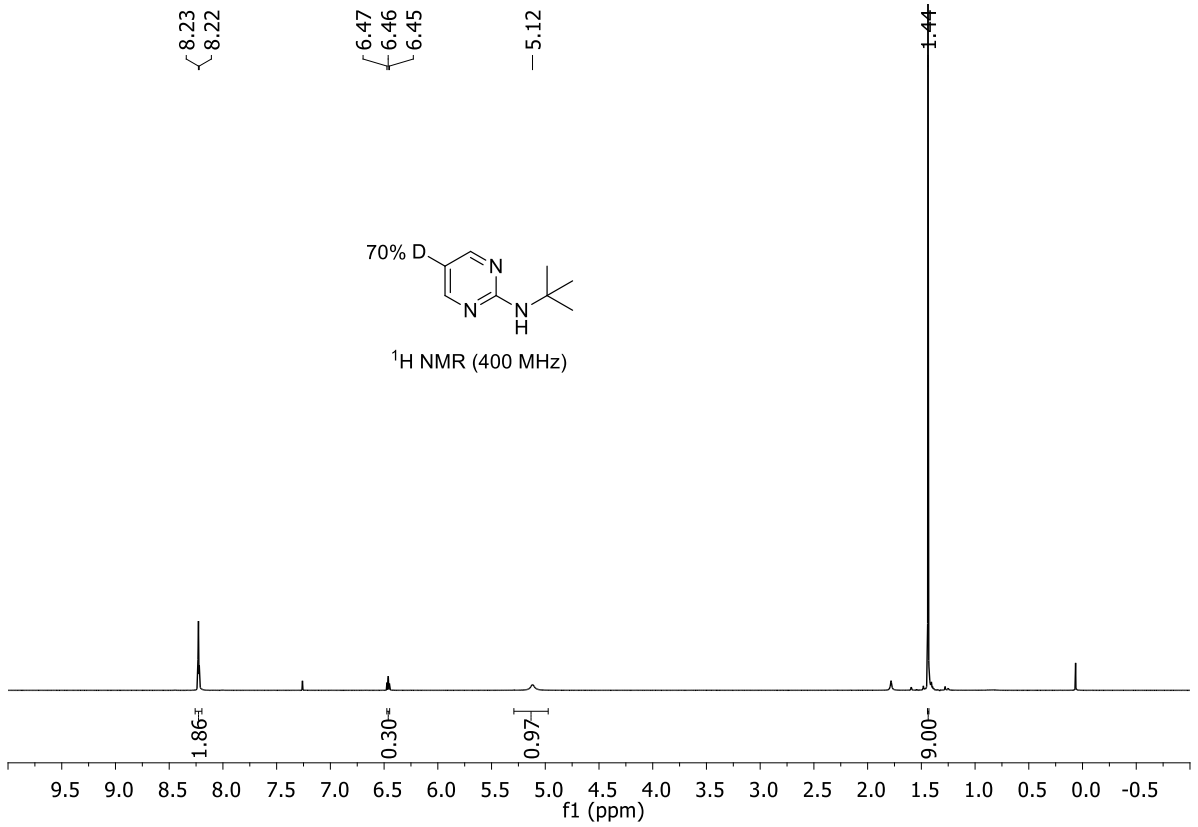
1i

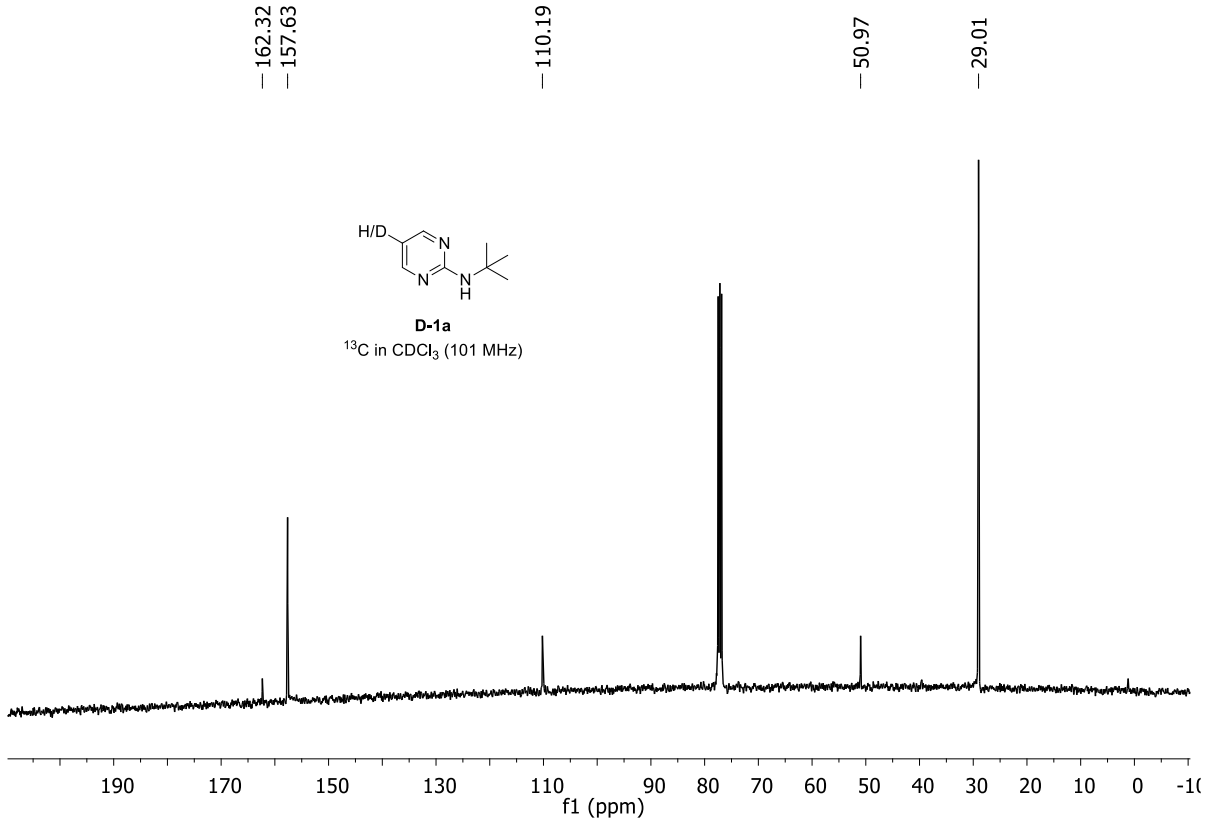
N-(*tert*-butyl)-5-iodopyrimidin-2-amine

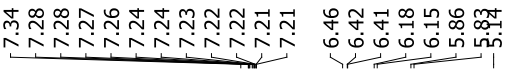
^{13}CNMR in $CDCl_3$ (101 MHz)

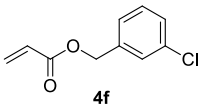

8.91
3.57
1.40
I
N
N
N
MeO
O
1j
methyl tert-butyl(5-iodopyrimidin-2-yl)carbamate
1H NMR in CDCl3 (400 MHz)
1.81
3.00
9.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.17
159.82
154.63
91.37
58.26
52.61
28.79
I
N
N
N
MeO
O
1j
methyl tert-butyl(5-iodopyrimidin-2-yl)carbamate
13C NMR in CDCl3 (126 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.23
8.22
6.47
6.46
6.45
5.12
1.44
70% D
N
N
N
H
1H NMR (400 MHz)
1.86
0.30
0.97
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


162.32
157.63
110.19
50.97
29.01
H/D
N
N
N
H
D-1a
13C in CDCl3 (101 MHz)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1(
f1 (ppm)

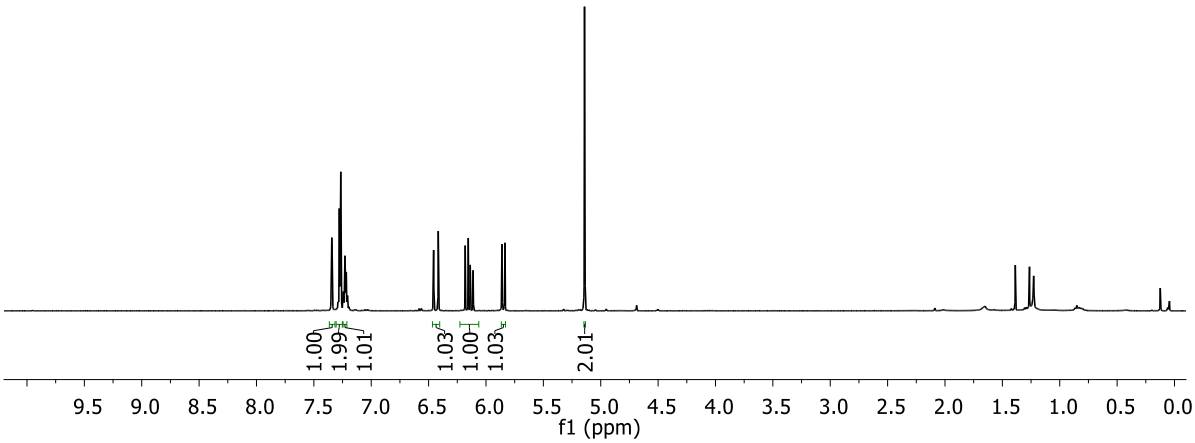


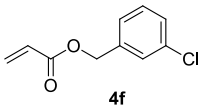


4f

3-chlorobenzyl acrylate

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

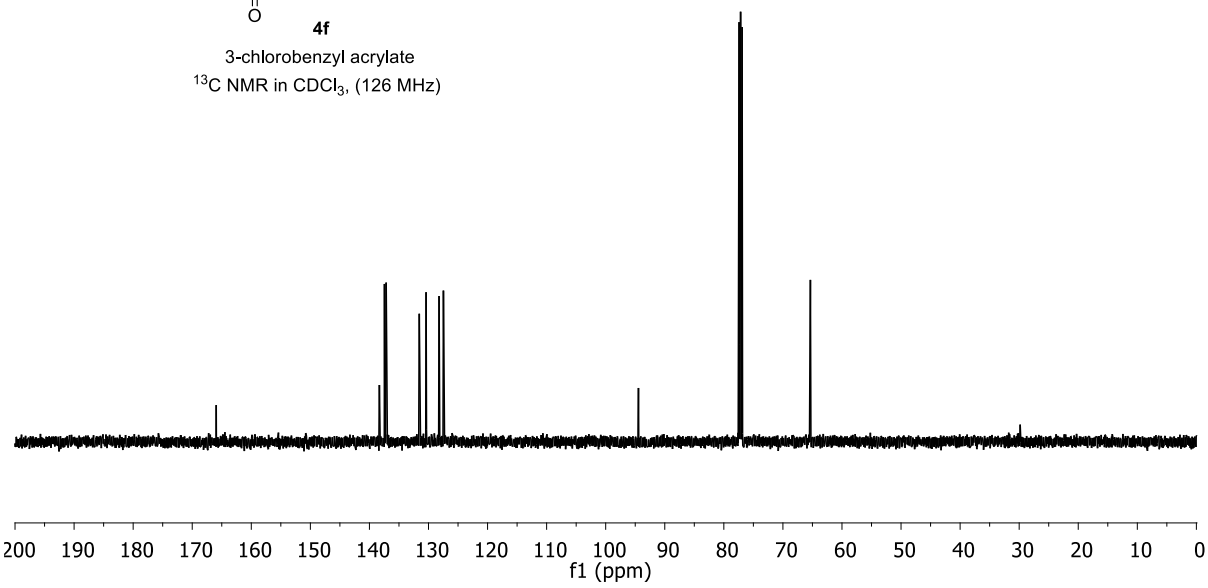


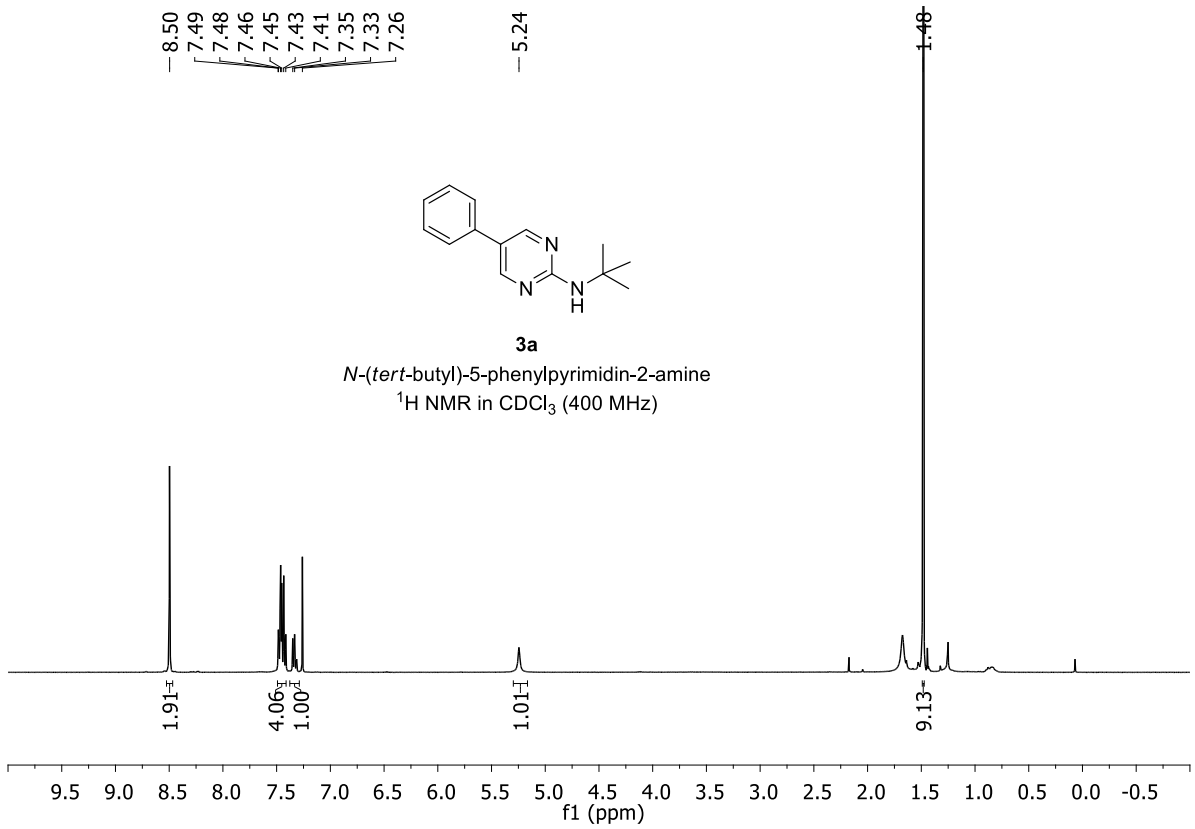


4f

3-chlorobenzyl acrylate

^{13}C NMR in $CDCl_3$, (126 MHz)

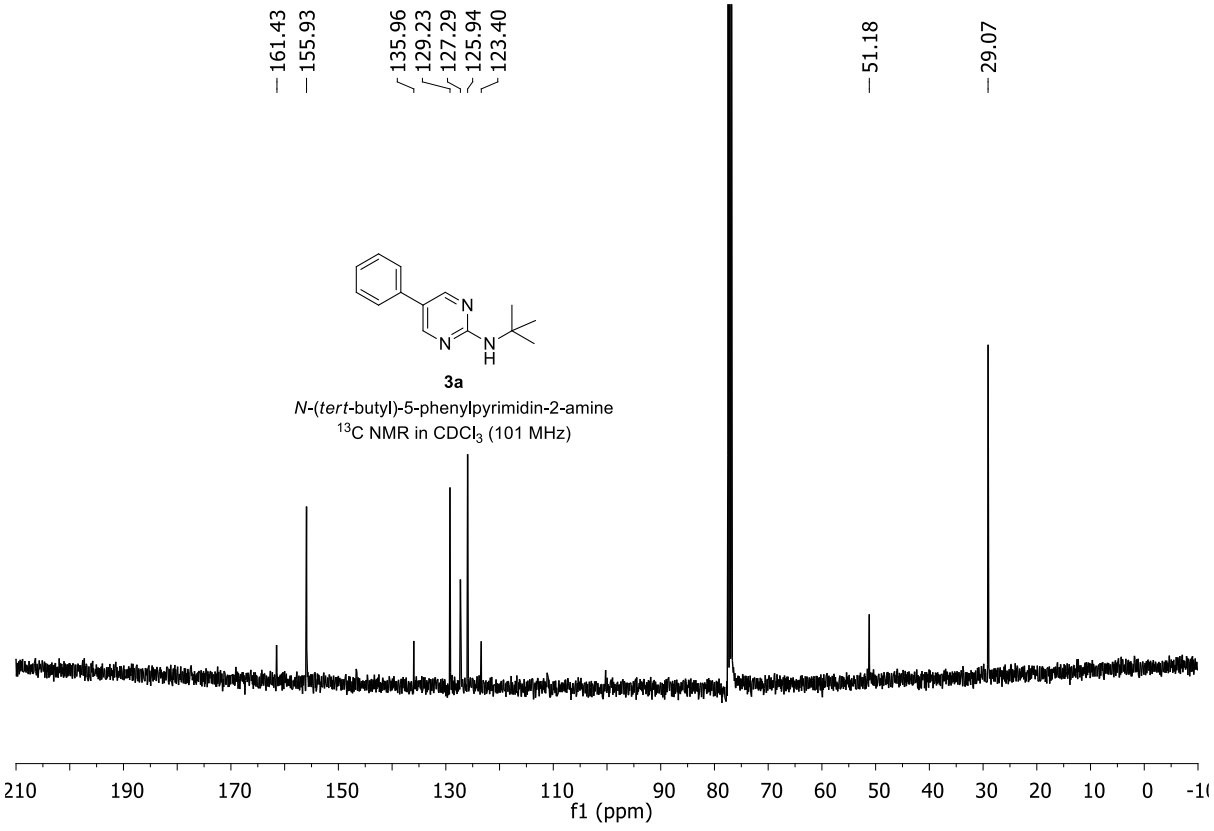




3a

N-(*tert*-butyl)-5-phenylpyrimidin-2-amine

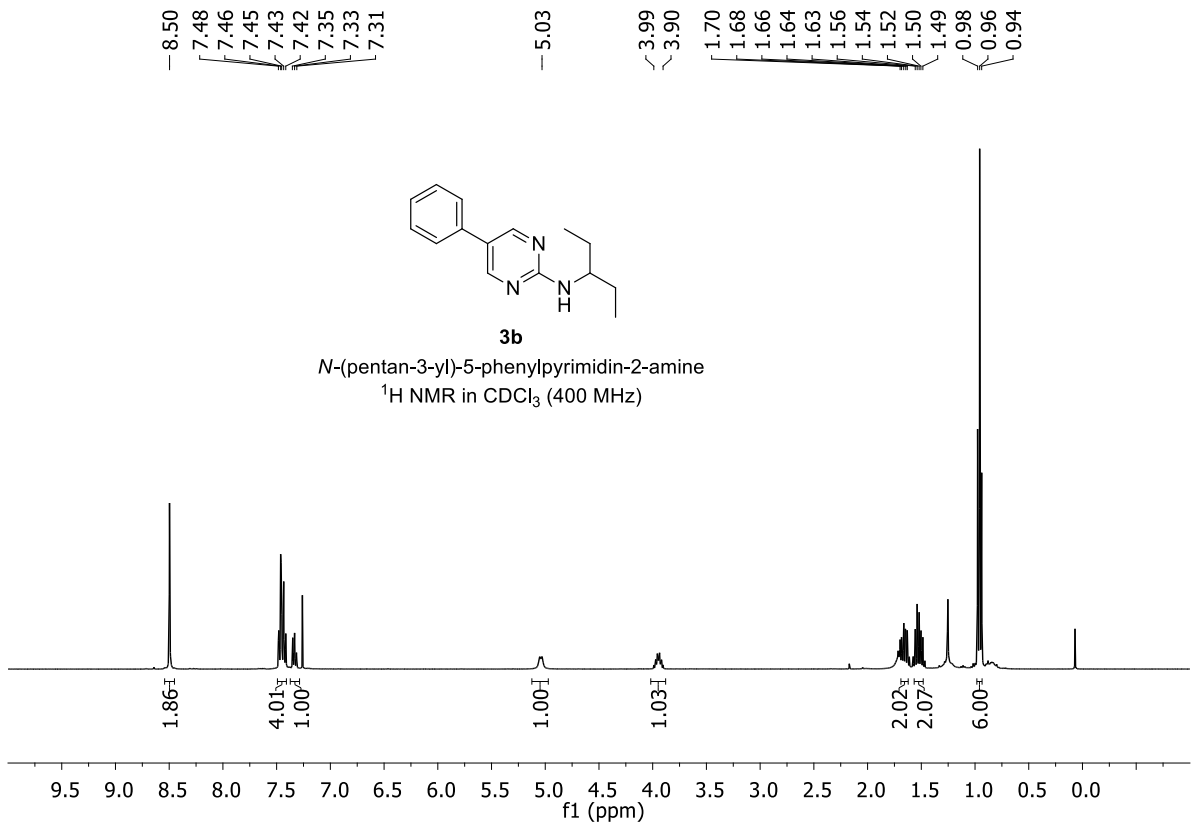
^{1}H NMR in $CDCl_3$ (400 MHz)



3a

N-(*tert*-butyl)-5-phenylpyrimidin-2-amine

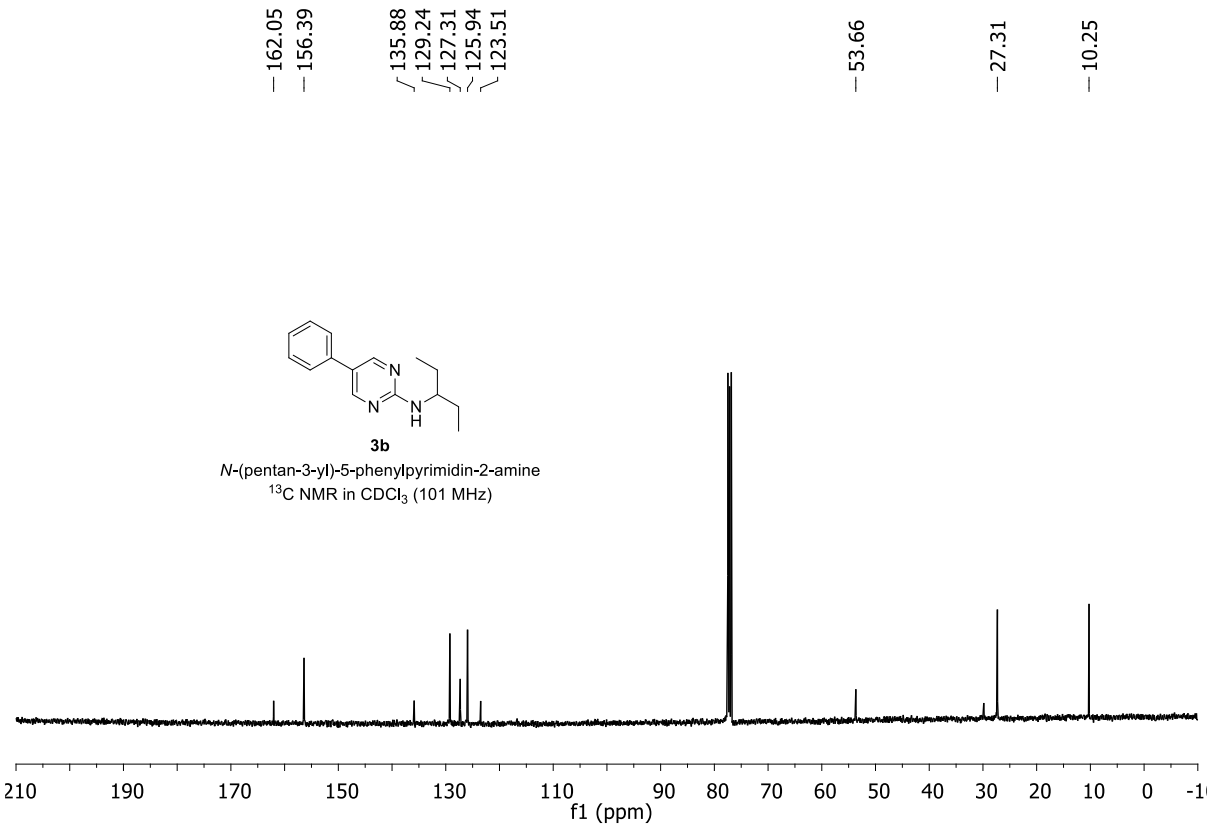
^{13}C NMR in $CDCl_3$ (101 MHz)



3b

N-(pentan-3-yl)-5-phenylpyrimidin-2-amine

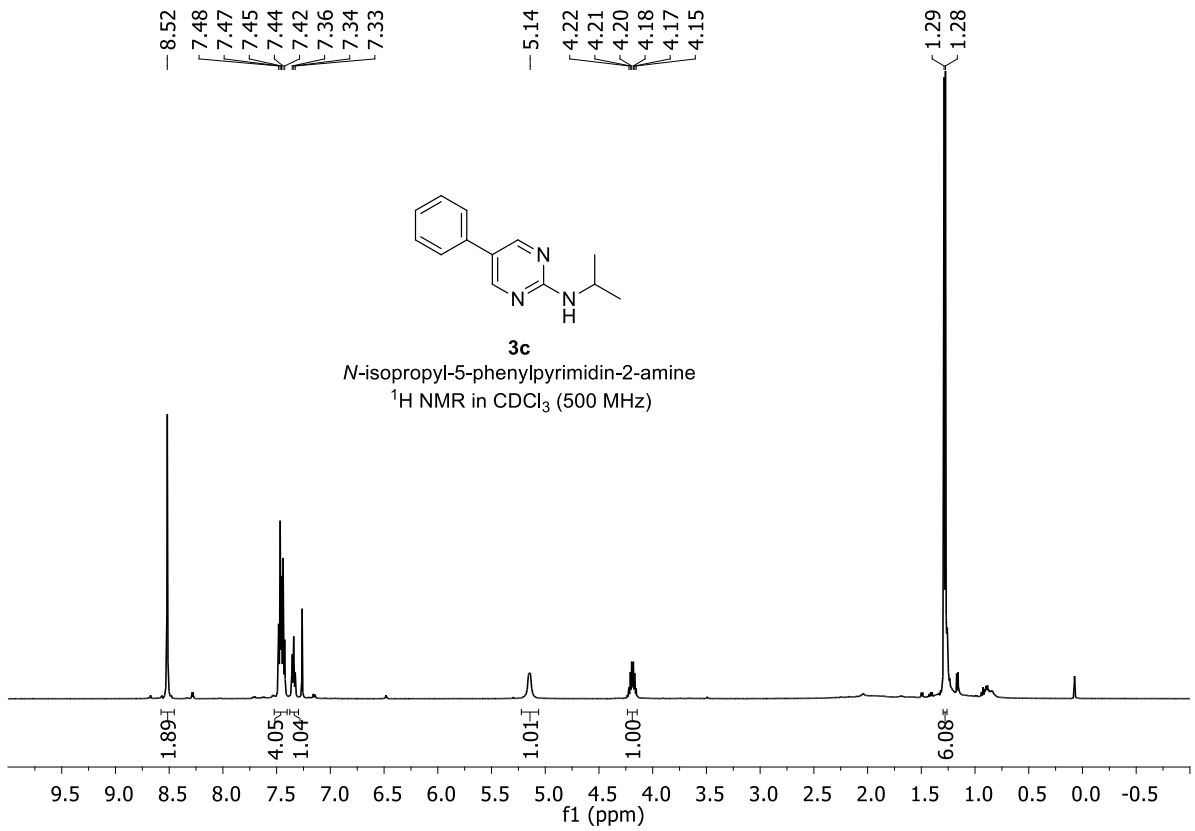
^{1}H NMR in $CDCl_3$ (400 MHz)



3b

N-(pentan-3-yl)-5-phenylpyrimidin-2-amine

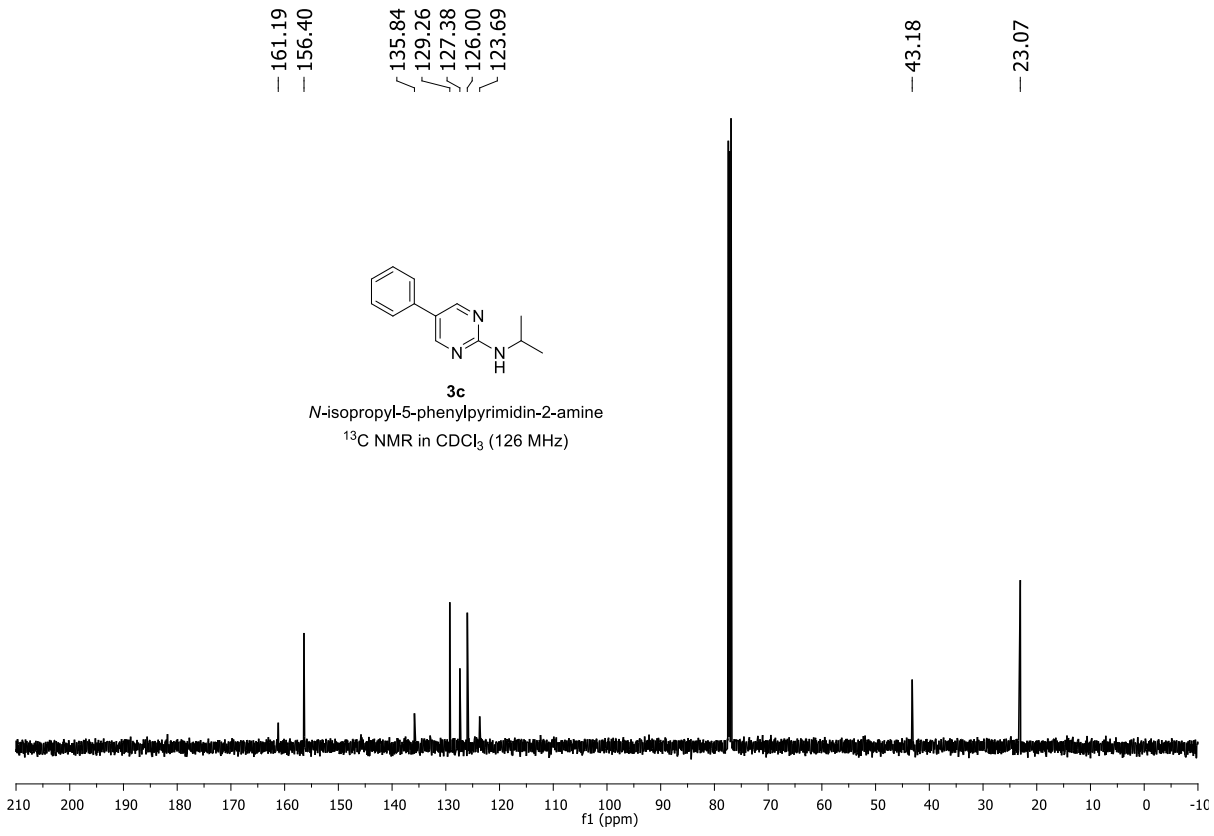
^{13}C NMR in $CDCl_3$ (101 MHz)



3c

N-isopropyl-5-phenylpyrimidin-2-amine

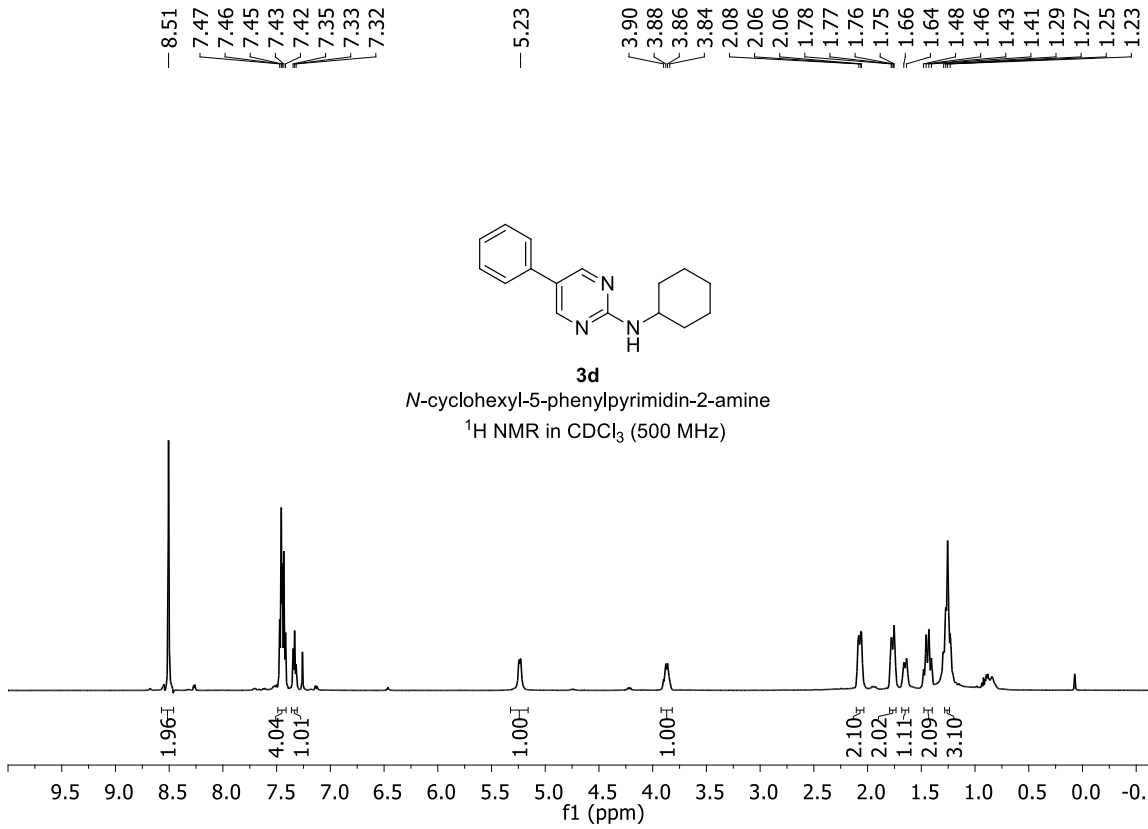
^{1}H NMR in $CDCl_3$ (500 MHz)

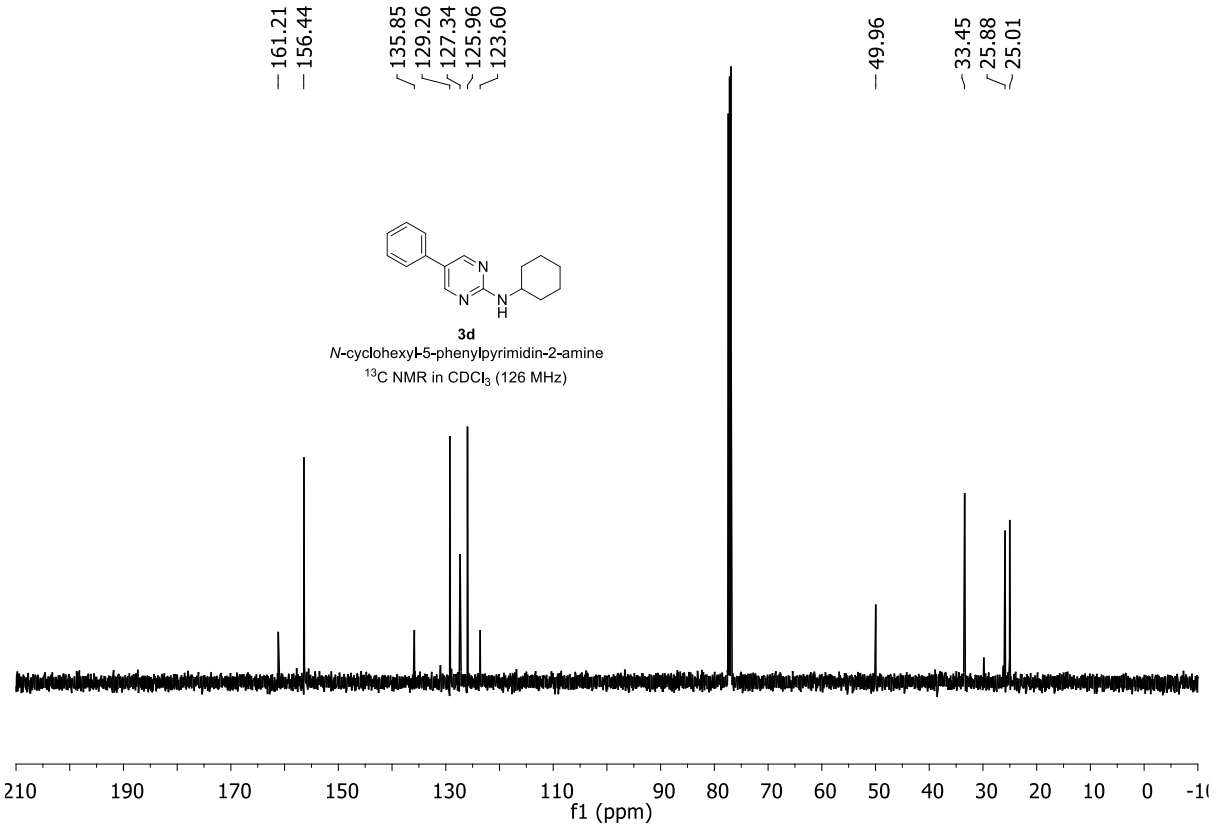


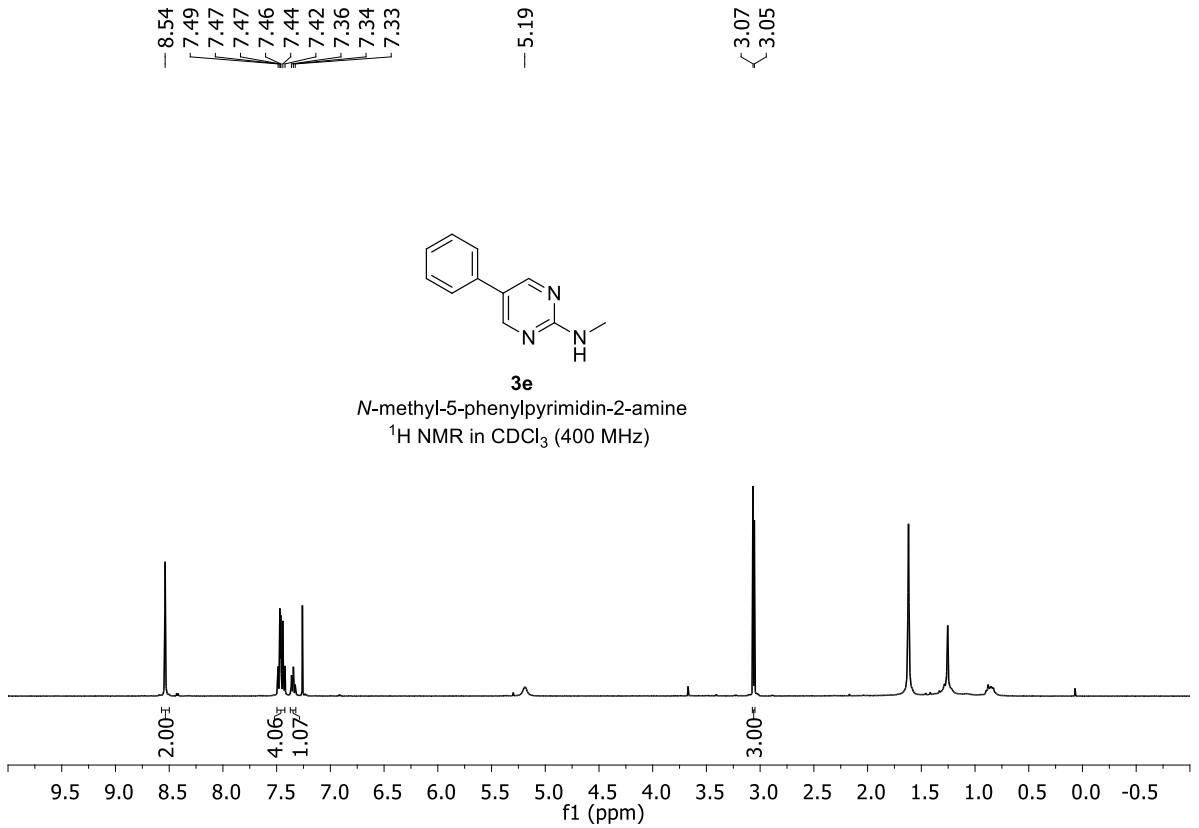
3c

N-isopropyl-5-phenylpyrimidin-2-amine

^{13}C NMR in $CDCl_3$ (126 MHz)


8.51
7.47
7.46
7.45
7.43
7.42
7.35
7.33
7.32
5.23
3.90
3.88
3.86
3.84
2.08
2.06
2.06
1.78
1.77
1.76
1.75
1.66
1.64
1.48
1.46
1.43
1.41
1.29
1.27
1.25
1.23
3d
N-cyclohexyl-5-phenylpyrimidin-2-amine
1H NMR in CDCl3 (500 MHz)
1.96
4.04
1.01
1.00
1.00
2.10
2.02
1.11
2.09
3.10
f1 (ppm)

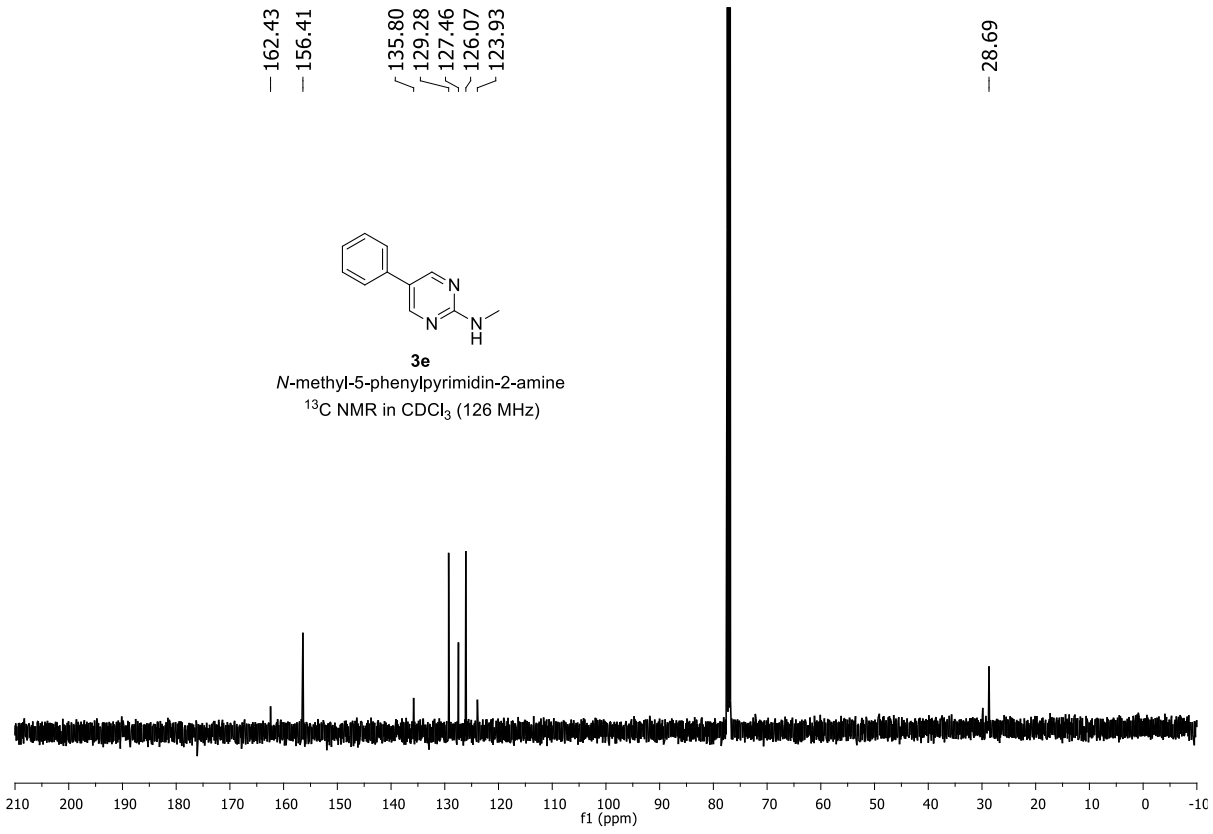

161.21
156.44
135.85
129.26
127.34
125.96
123.60
49.96
33.45
25.88
25.01
3d
N-cyclohexyl-5-phenylpyrimidin-2-amine
13C NMR in CDCl3 (126 MHz)
f1 (ppm)



3e

N-methyl-5-phenylpyrimidin-2-amine

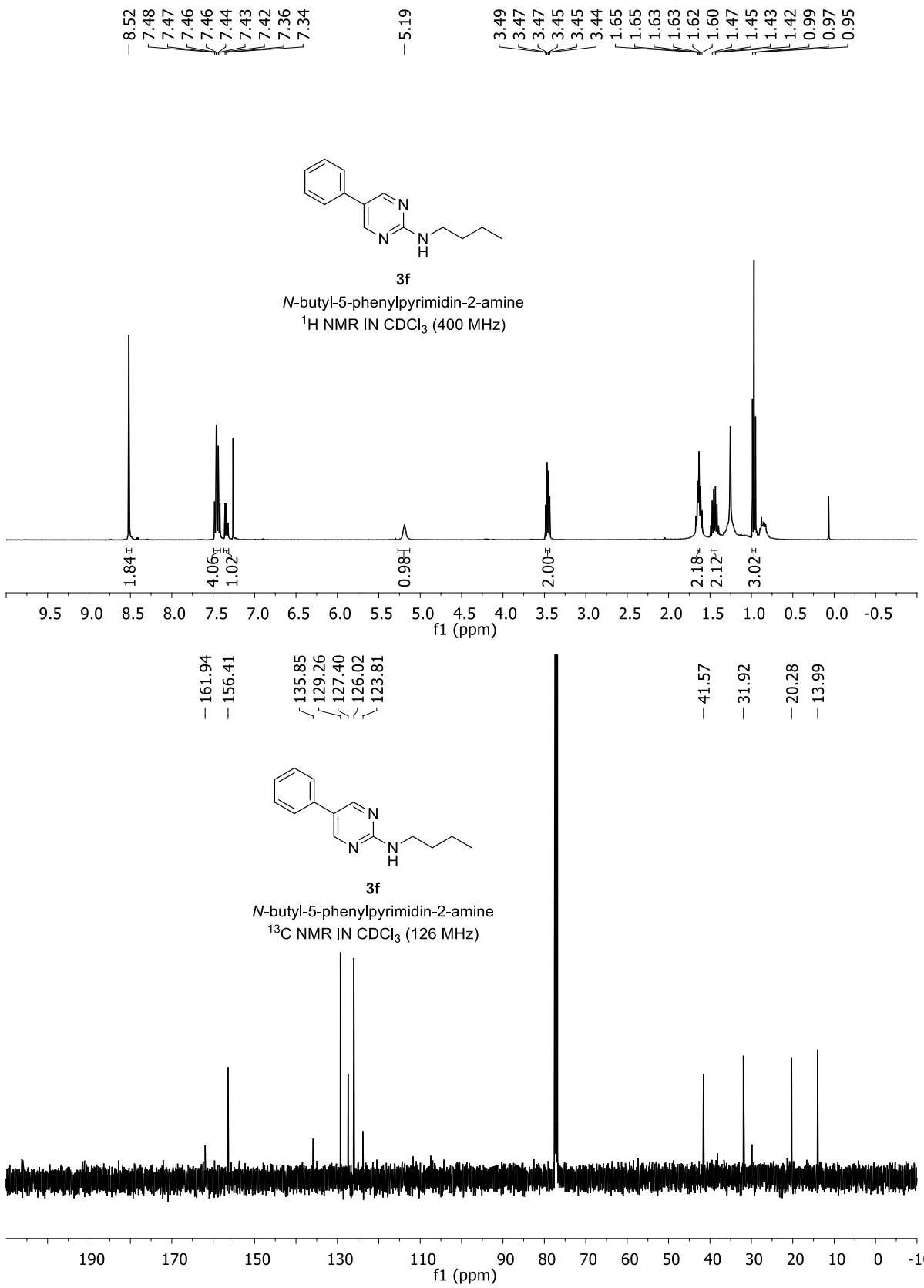
^{1}H NMR in $CDCl_3$ (400 MHz)

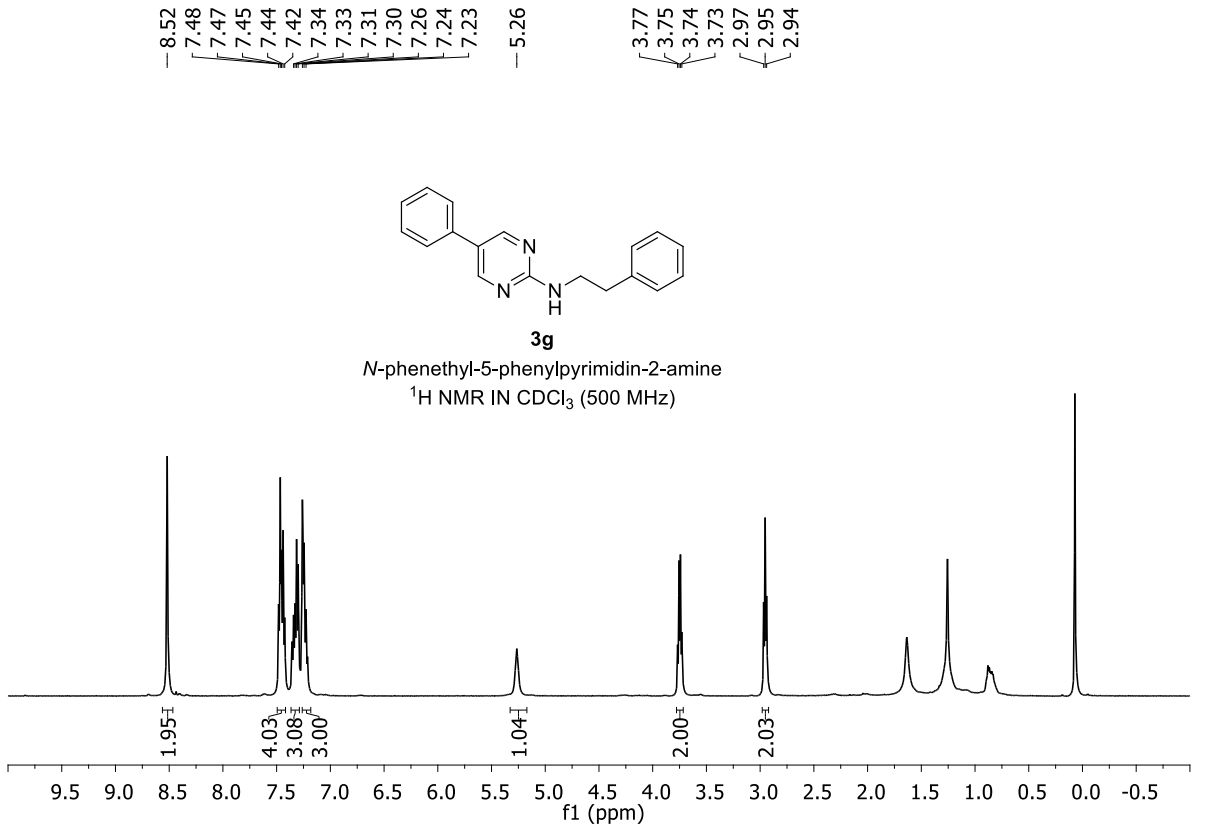


3e

N-methyl-5-phenylpyrimidin-2-amine

^{13}C NMR in $CDCl_3$ (126 MHz)

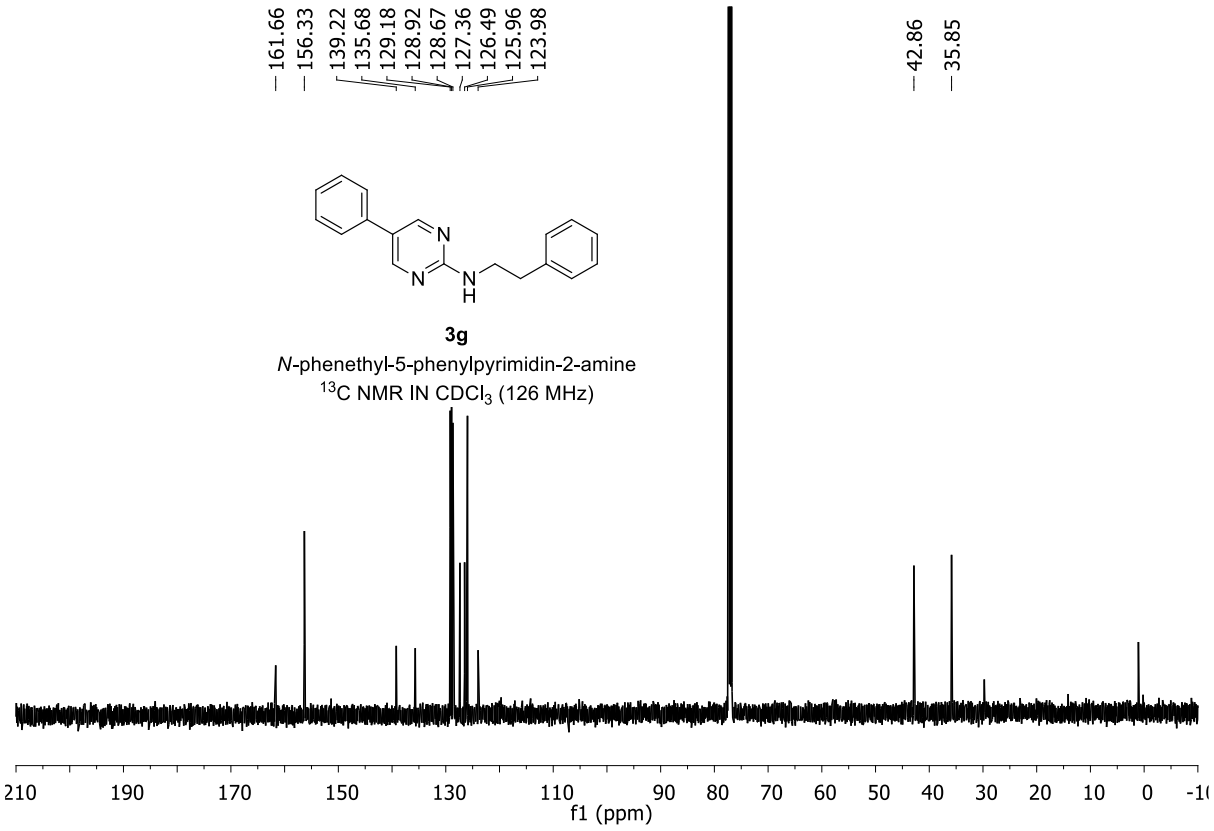

8.52
7.48
7.47
7.46
7.46
7.44
7.43
7.42
7.36
7.34
5.19
3.49
3.47
3.47
3.45
3.45
3.44
1.65
1.65
1.63
1.63
1.62
1.60
1.47
1.45
1.43
1.42
0.99
0.97
0.95
3f
N-butyl-5-phenylpyrimidin-2-amine
1H NMR IN CDCl3 (400 MHz)
1.84
4.06
1.02
0.98
2.00
2.18
2.12
3.02
f1 (ppm)
161.94
156.41
135.85
129.26
127.40
126.02
123.81
41.57
31.92
20.28
13.99
3f
N-butyl-5-phenylpyrimidin-2-amine
13C NMR IN CDCl3 (126 MHz)
f1 (ppm)



3g

N-phenethyl-5-phenylpyrimidin-2-amine

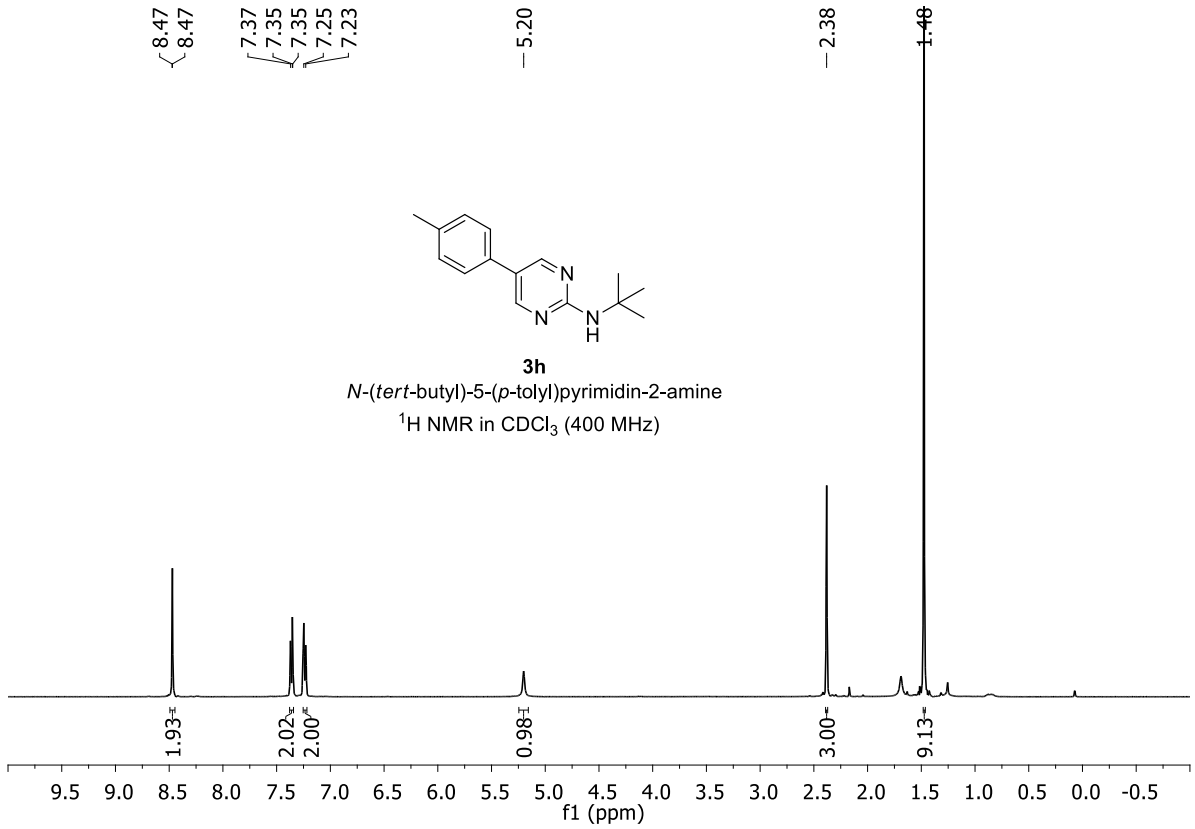
^{1}H NMR IN $CDCl_3$ (500 MHz)



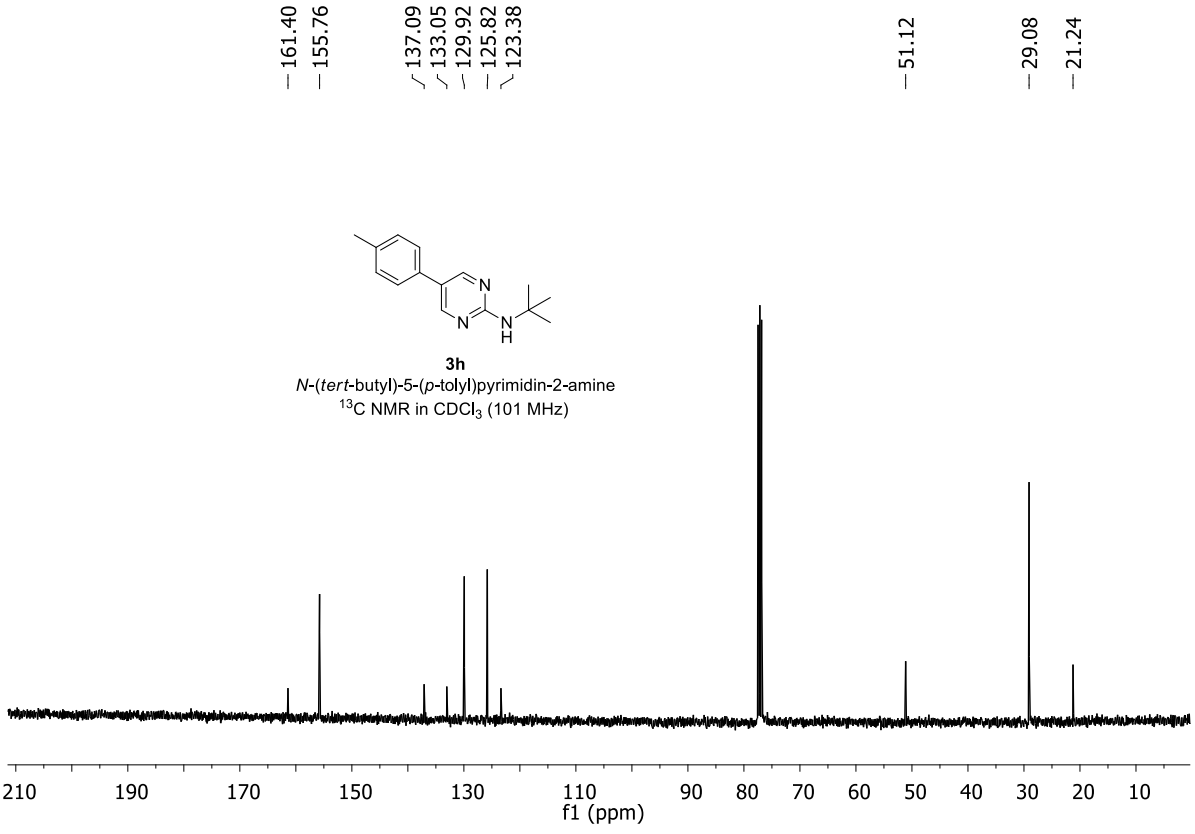
3g

N-phenethyl-5-phenylpyrimidin-2-amine

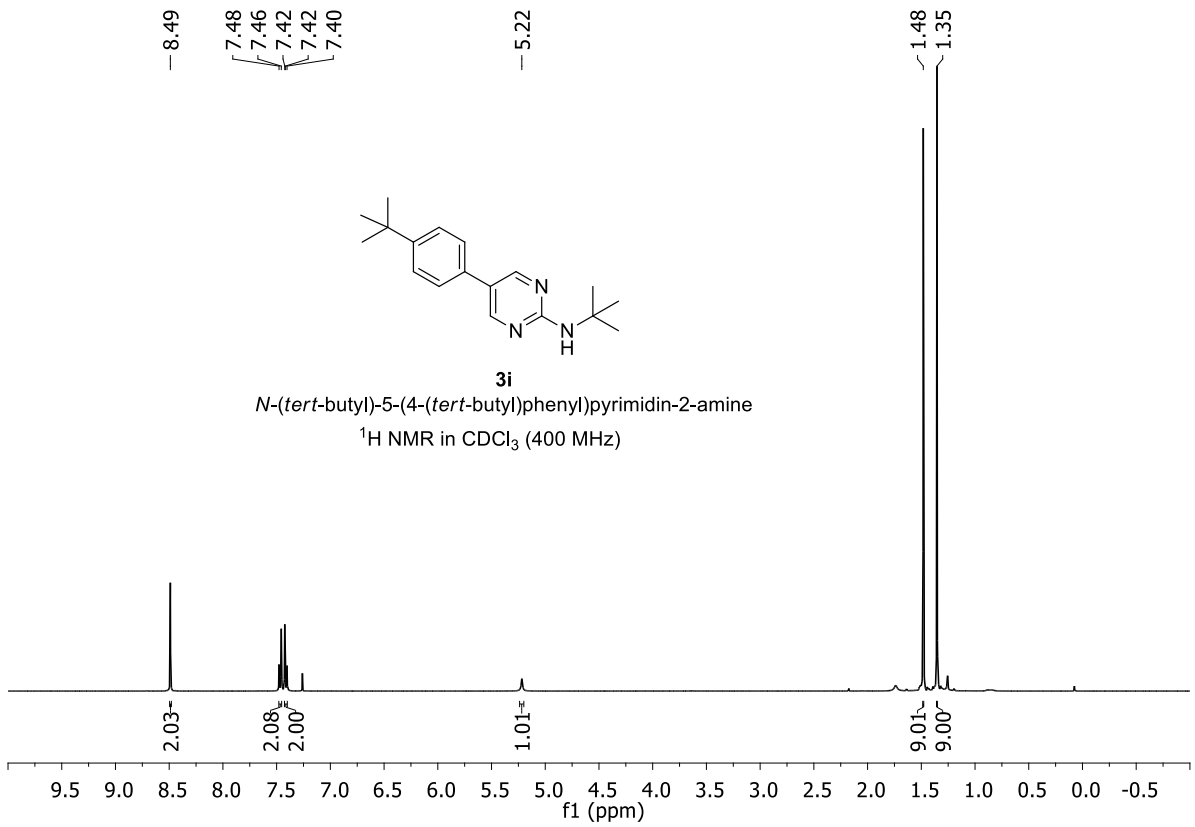
^{13}C NMR IN $CDCl_3$ (126 MHz)



3h
N-(*tert*-butyl)-5-(*p*-tolyl)pyrimidin-2-amine
^{1}H NMR in $CDCl_3$ (400 MHz)



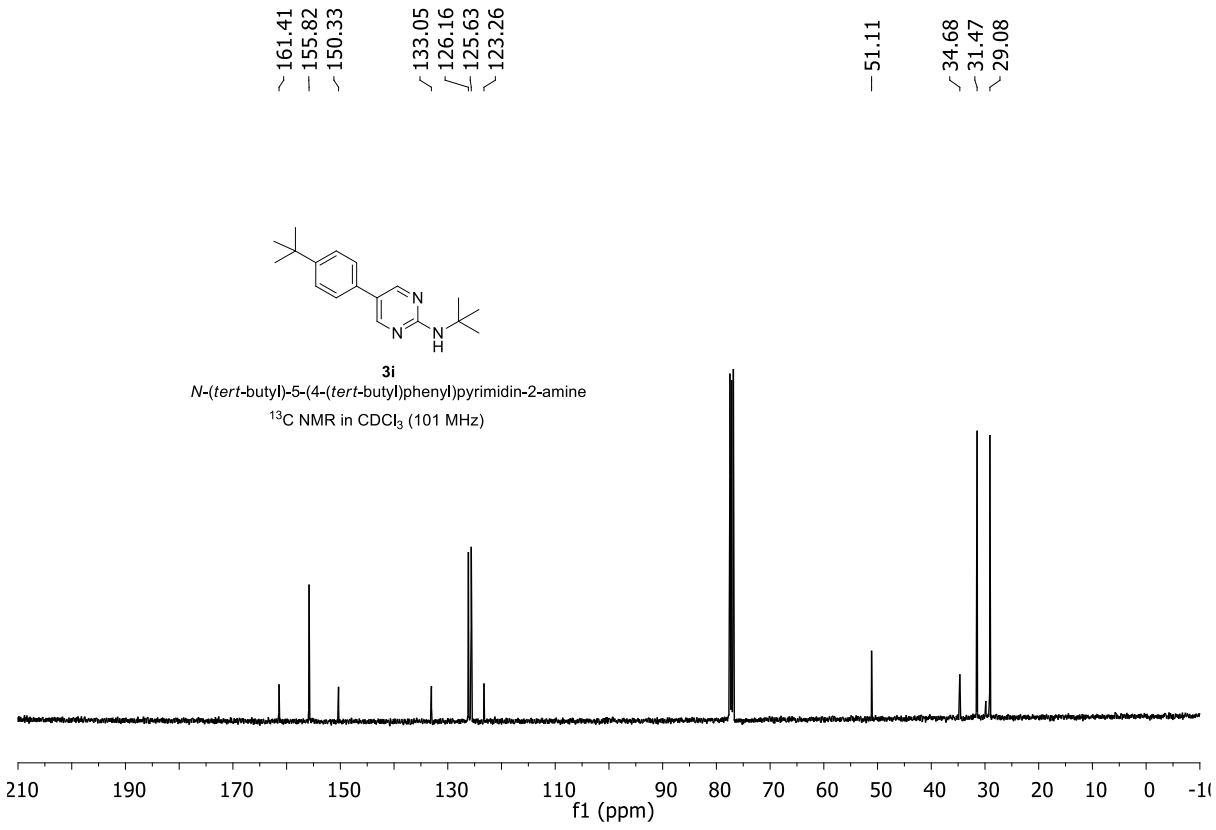
3h
N-(*tert*-butyl)-5-(*p*-tolyl)pyrimidin-2-amine
^{13}C NMR in $CDCl_3$ (101 MHz)



3i

N-(*tert*-butyl)-5-(4-(*tert*-butyl)phenyl)pyrimidin-2-amine

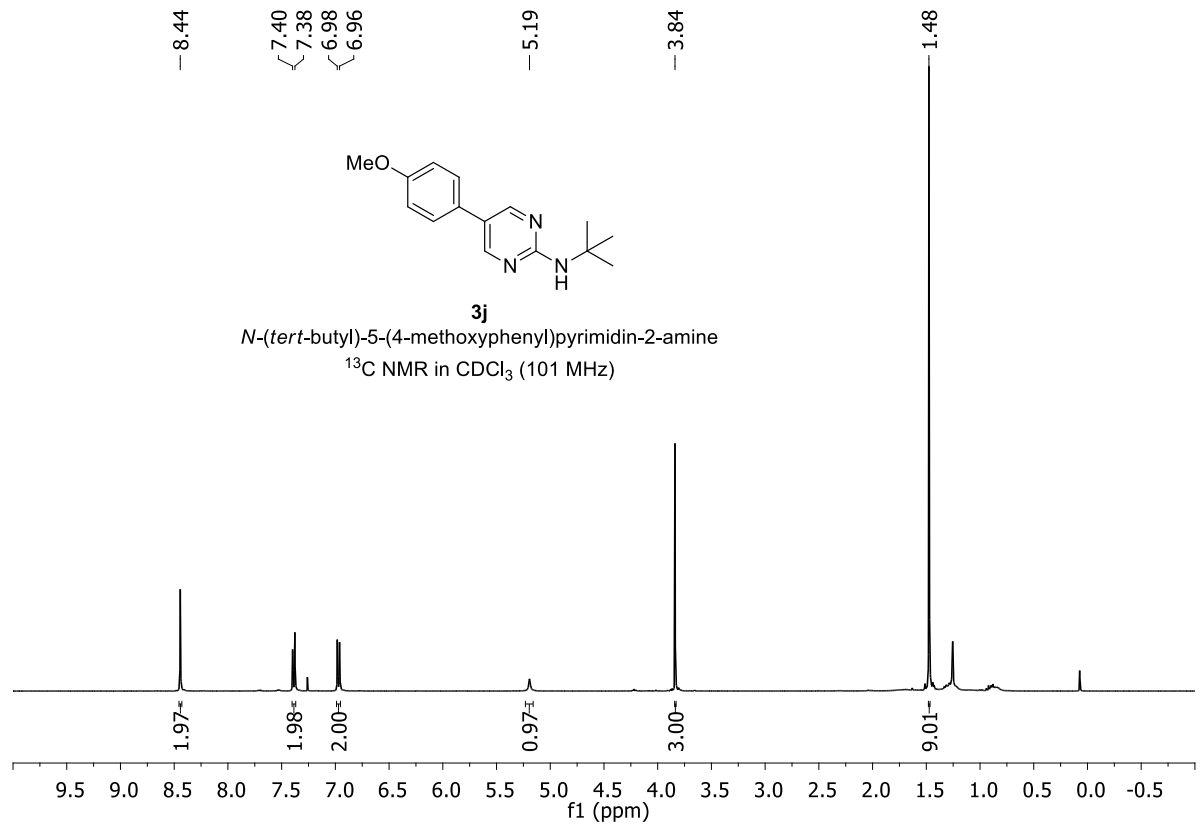
^{1}H NMR in $CDCl_3$ (400 MHz)



3i

N-(*tert*-butyl)-5-(4-(*tert*-butyl)phenyl)pyrimidin-2-amine

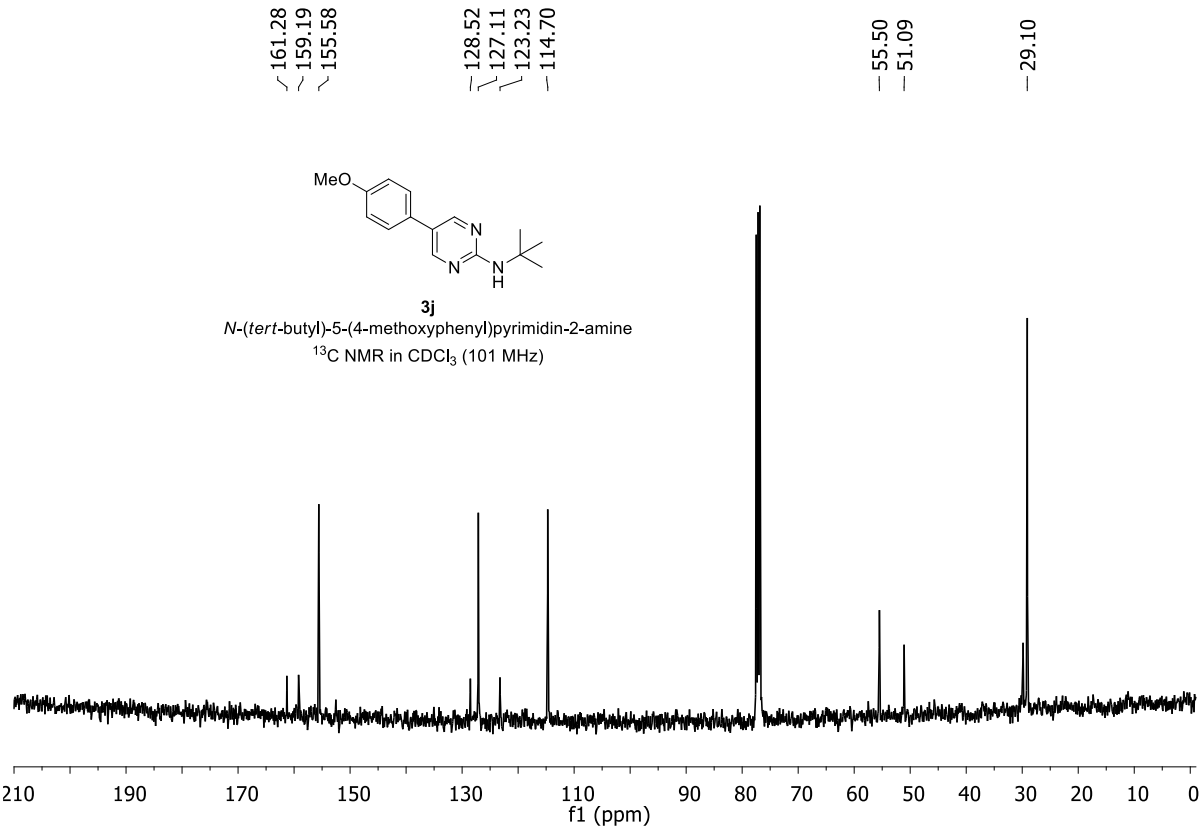
^{13}C NMR in $CDCl_3$ (101 MHz)



3j

N-(*tert*-butyl)-5-(4-methoxyphenyl)pyrimidin-2-amine

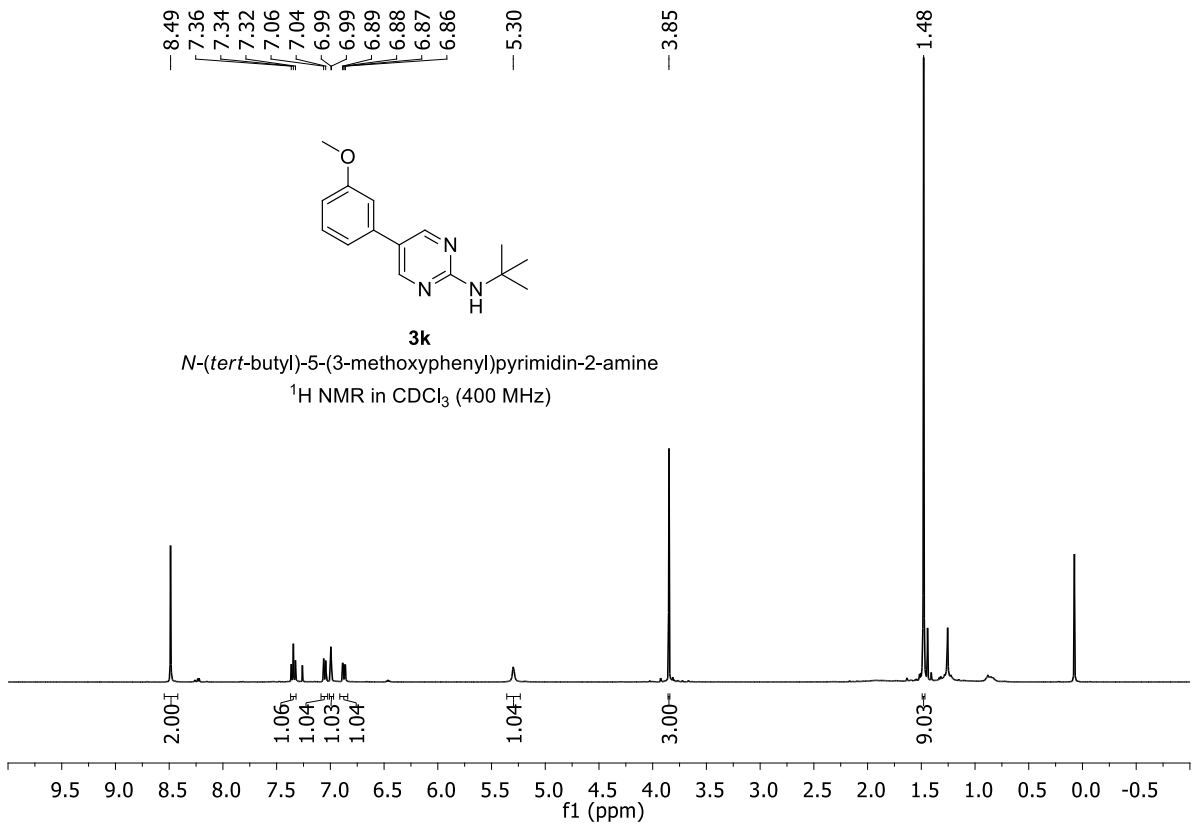
^{13}C NMR in $CDCl_3$ (101 MHz)



3j

N-(*tert*-butyl)-5-(4-methoxyphenyl)pyrimidin-2-amine

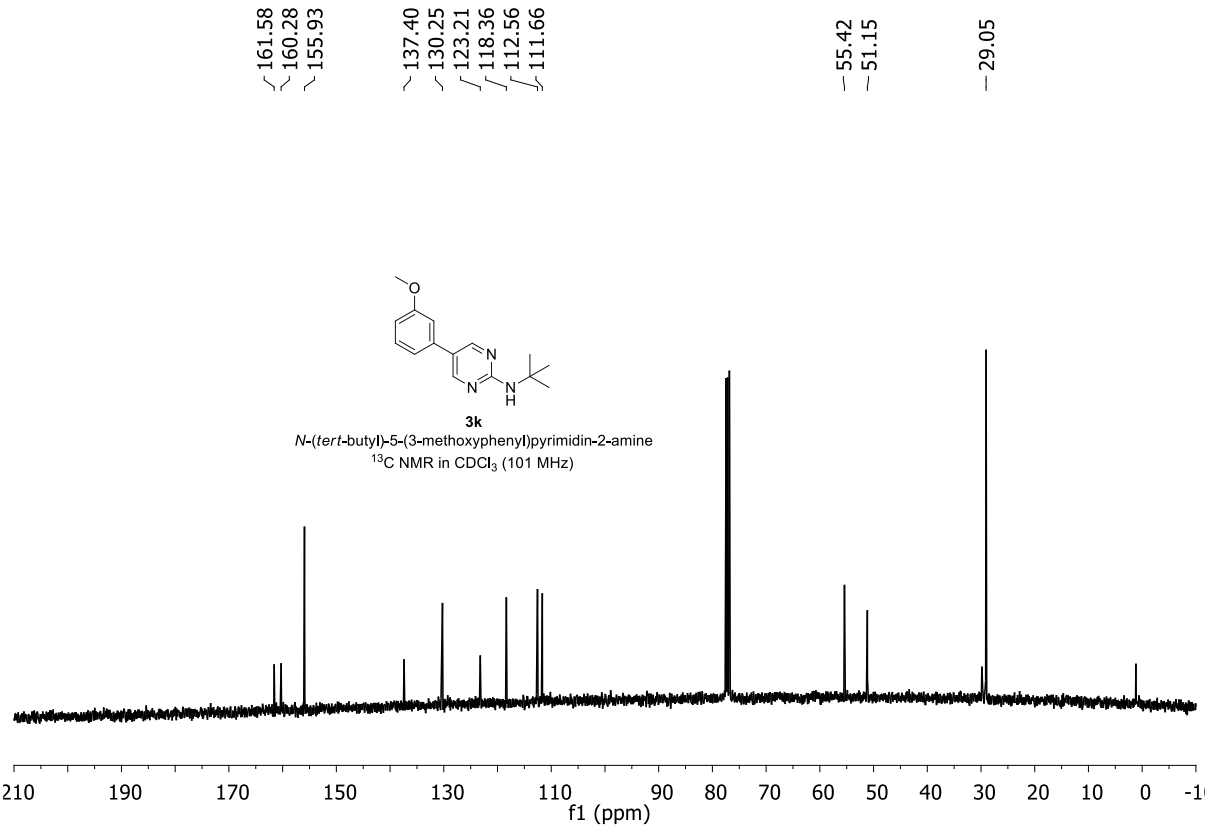
^{13}C NMR in $CDCl_3$ (101 MHz)



3k

N-(*tert*-butyl)-5-(3-methoxyphenyl)pyrimidin-2-amine

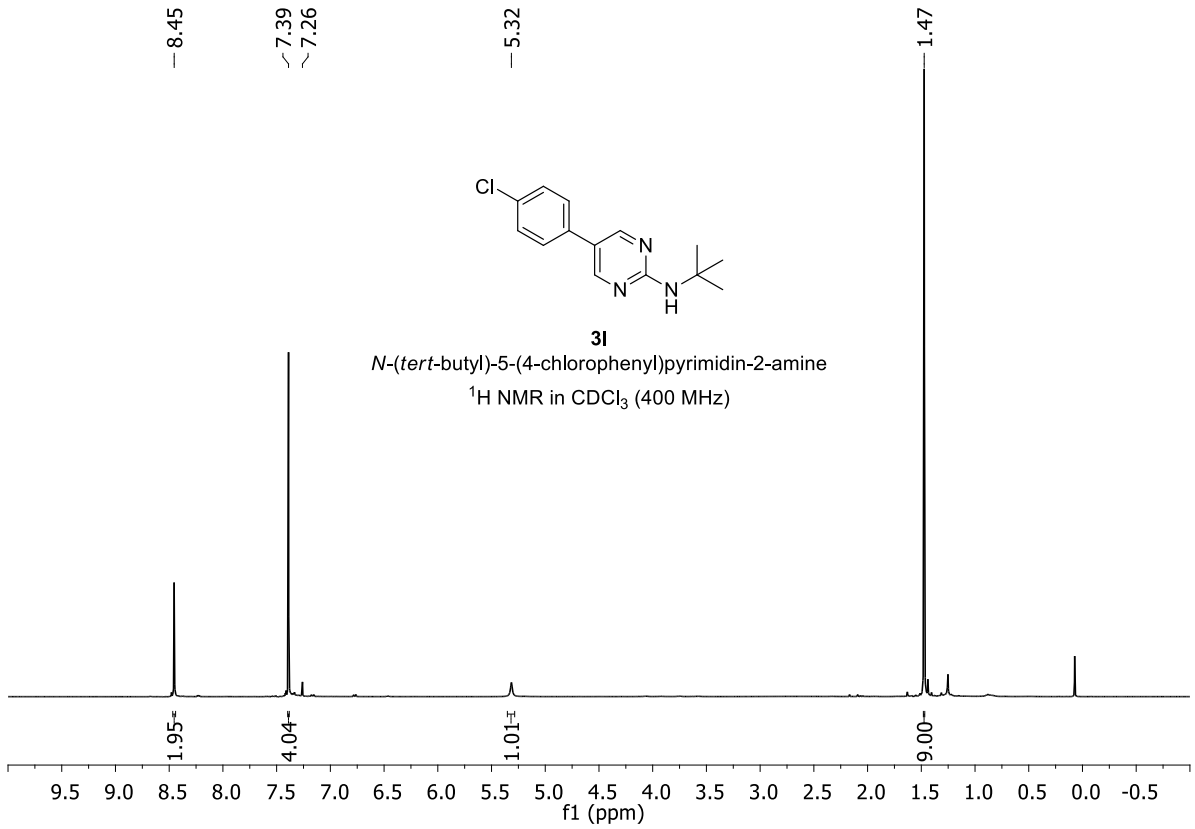
^{1}H NMR in $CDCl_3$ (400 MHz)



3k

N-(*tert*-butyl)-5-(3-methoxyphenyl)pyrimidin-2-amine

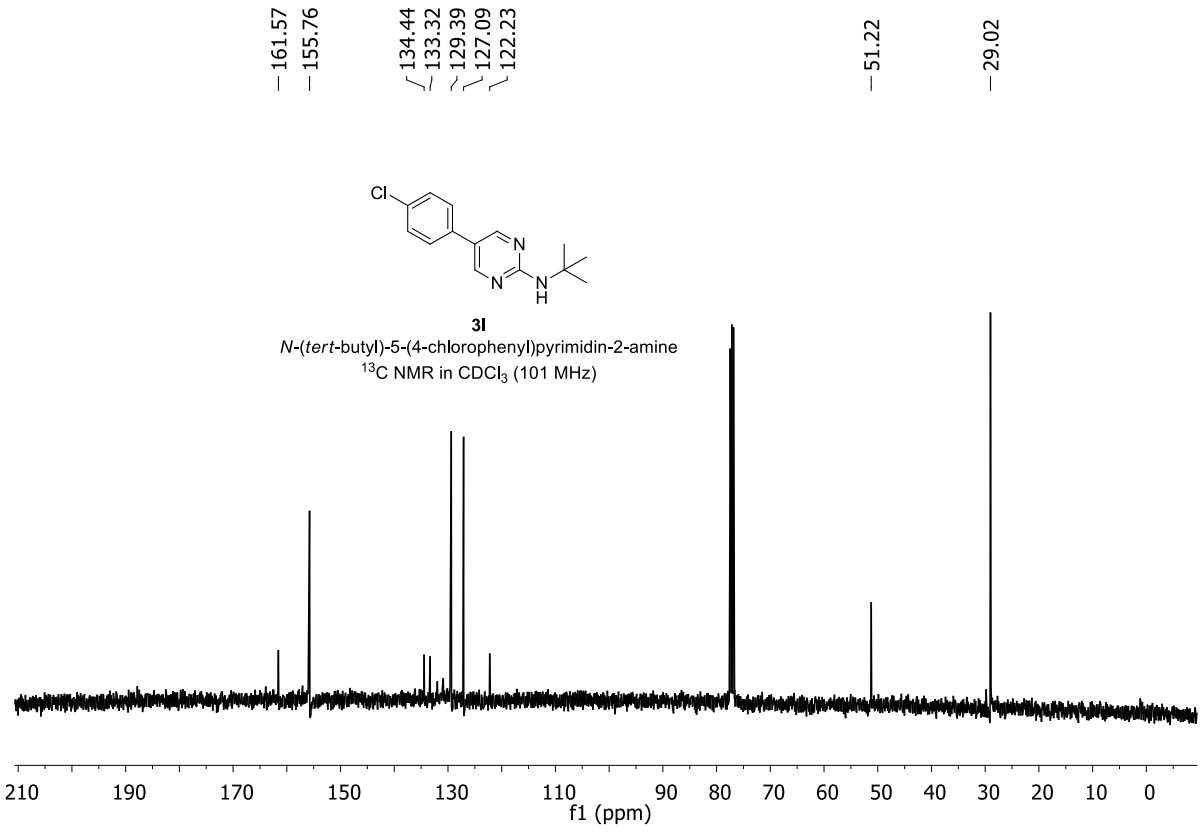
^{13}C NMR in $CDCl_3$ (101 MHz)



3l

N-(*tert*-butyl)-5-(4-chlorophenyl)pyrimidin-2-amine

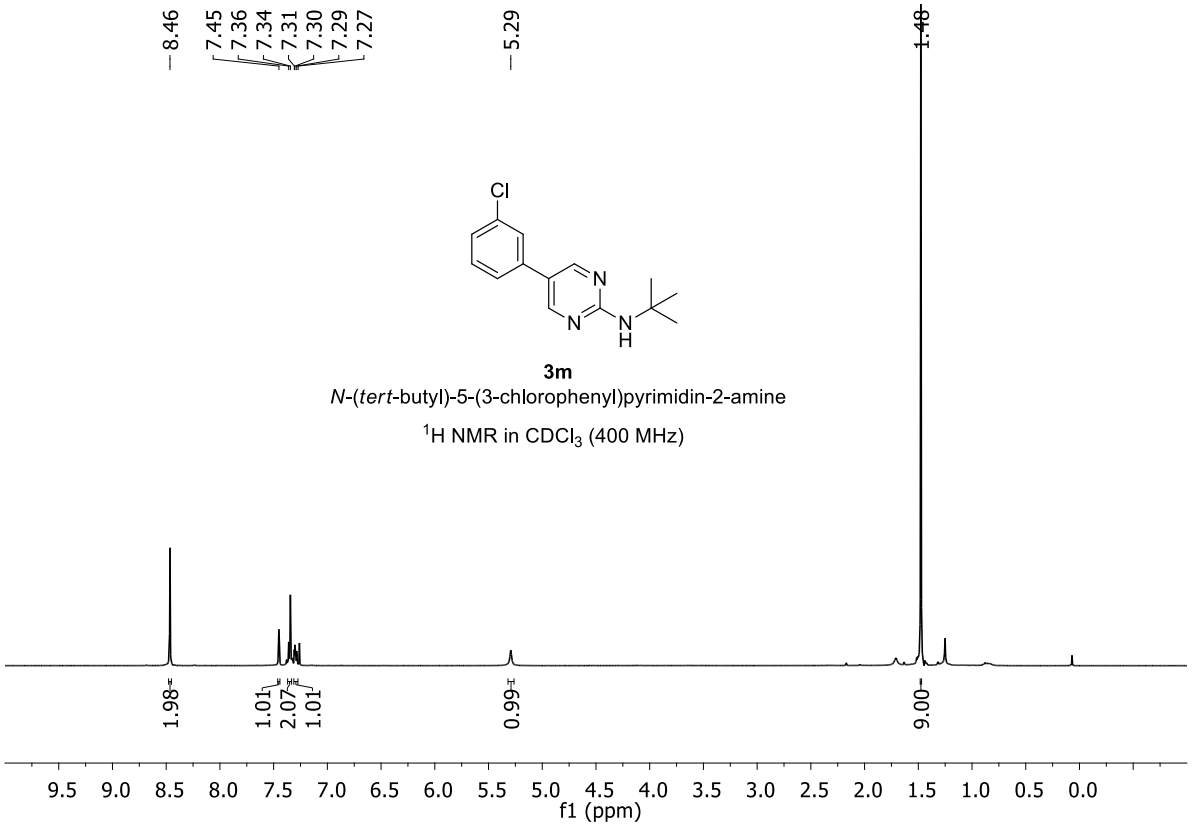
^{1}H NMR in $CDCl_3$ (400 MHz)



3l

N-(*tert*-butyl)-5-(4-chlorophenyl)pyrimidin-2-amine

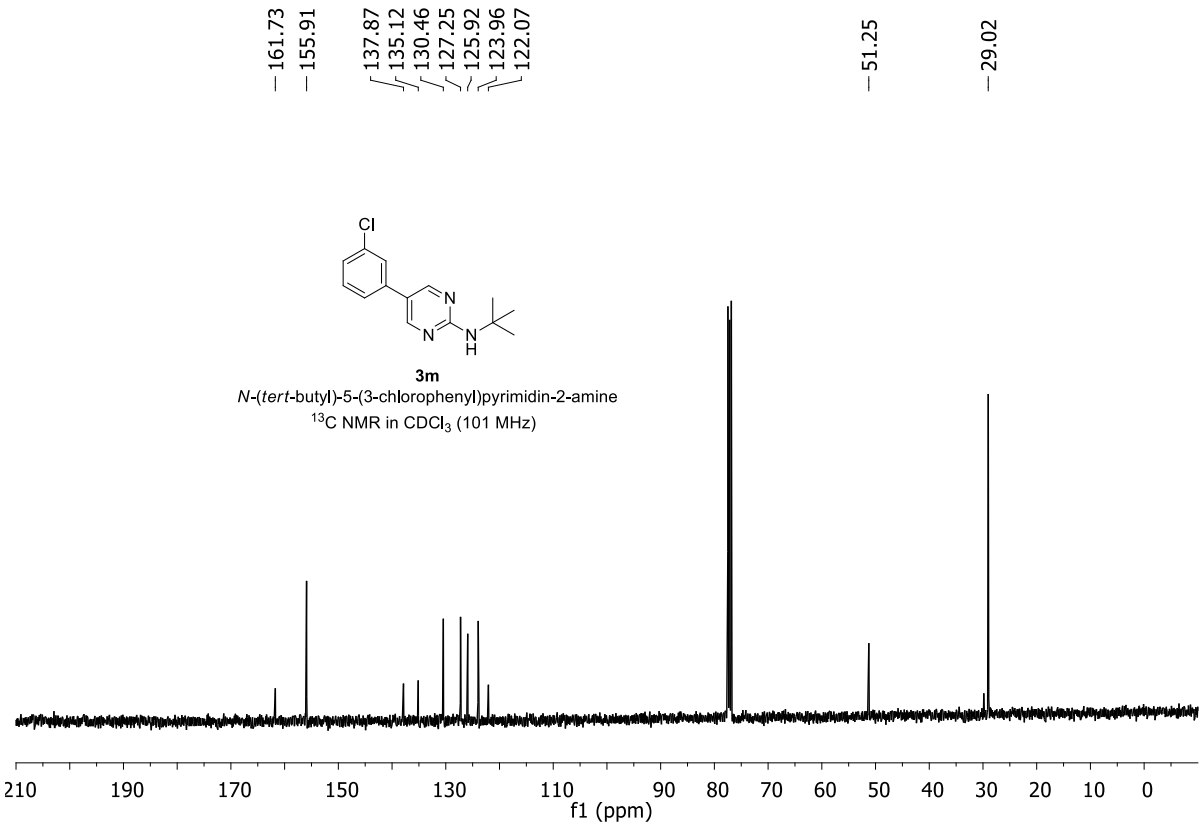
^{13}C NMR in $CDCl_3$ (101 MHz)



3m

N-(*tert*-butyl)-5-(3-chlorophenyl)pyrimidin-2-amine

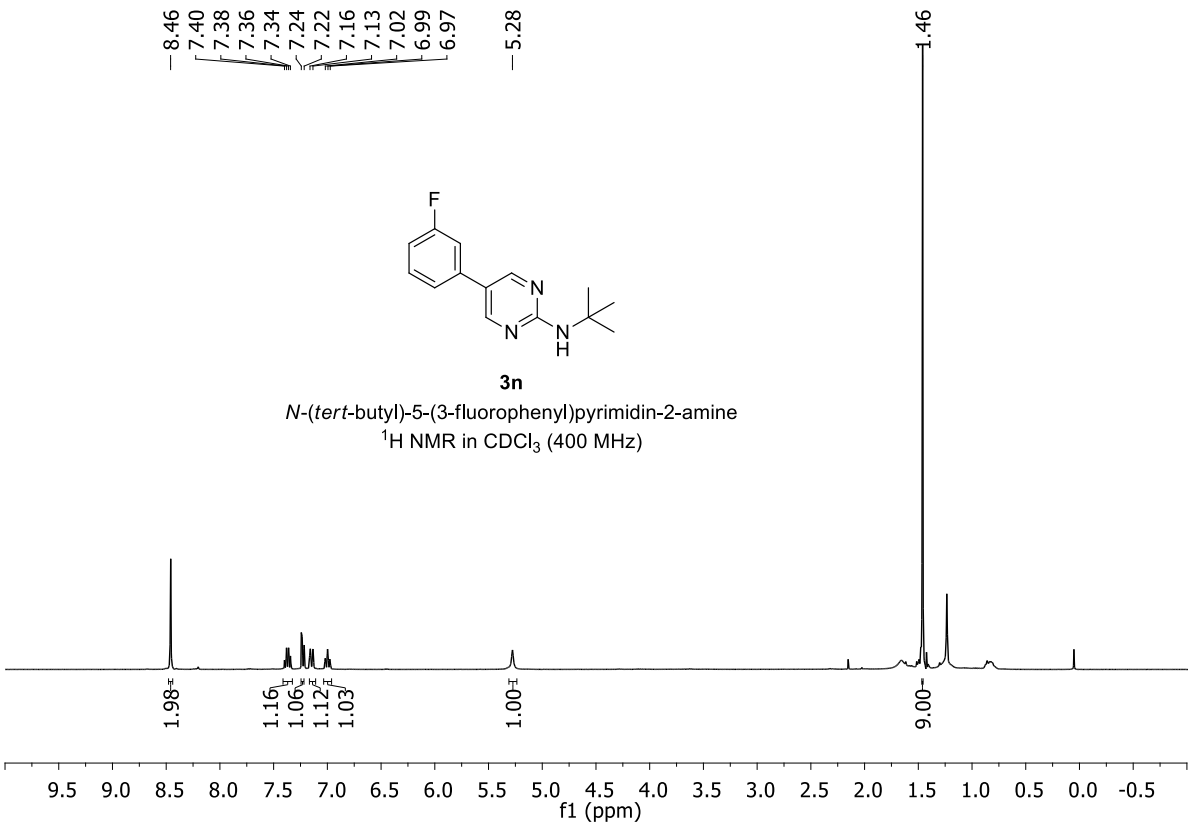
^{1}H NMR in $CDCl_3$ (400 MHz)



3m

N-(*tert*-butyl)-5-(3-chlorophenyl)pyrimidin-2-amine

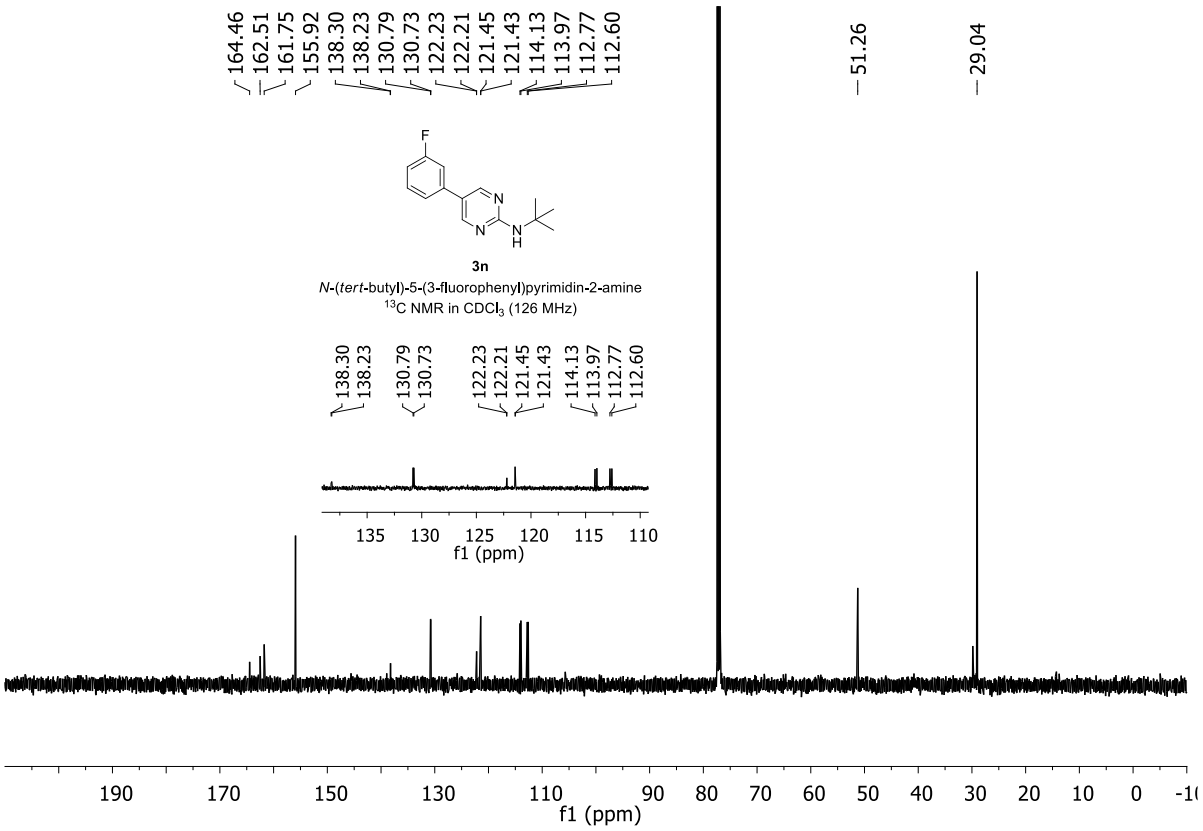
^{13}C NMR in $CDCl_3$ (101 MHz)



3n

N-(*tert*-butyl)-5-(3-fluorophenyl)pyrimidin-2-amine

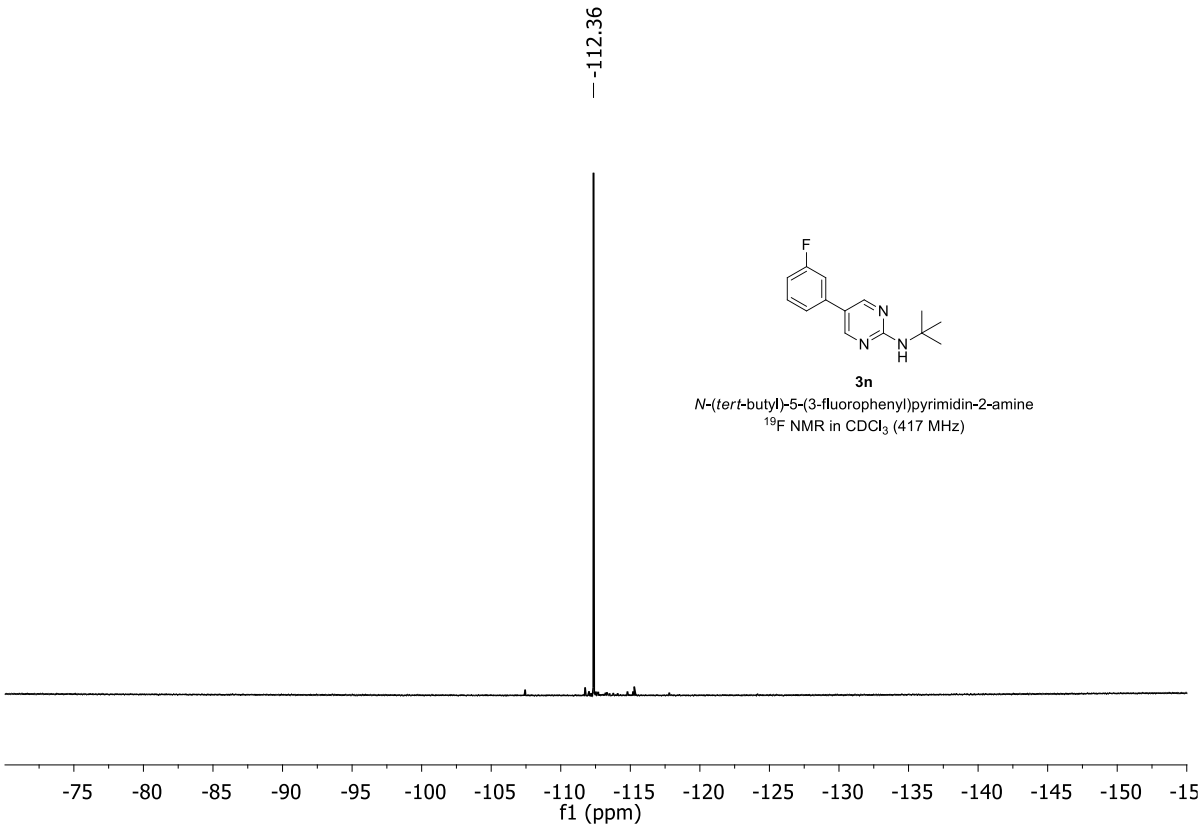
^{1}H NMR in $CDCl_3$ (400 MHz)



3n

N-(*tert*-butyl)-5-(3-fluorophenyl)pyrimidin-2-amine

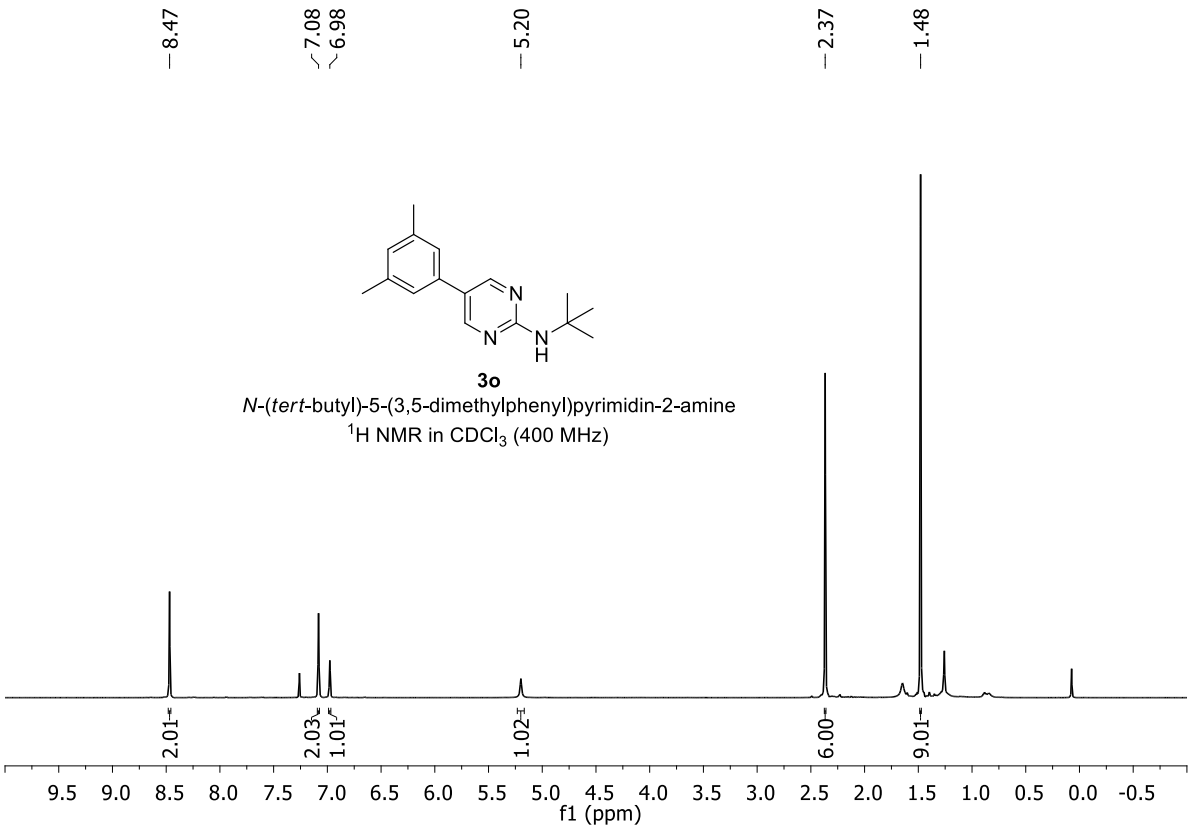
^{13}C NMR in $CDCl_3$ (126 MHz)



3n

N-(*tert*-butyl)-5-(3-fluorophenyl)pyrimidin-2-amine

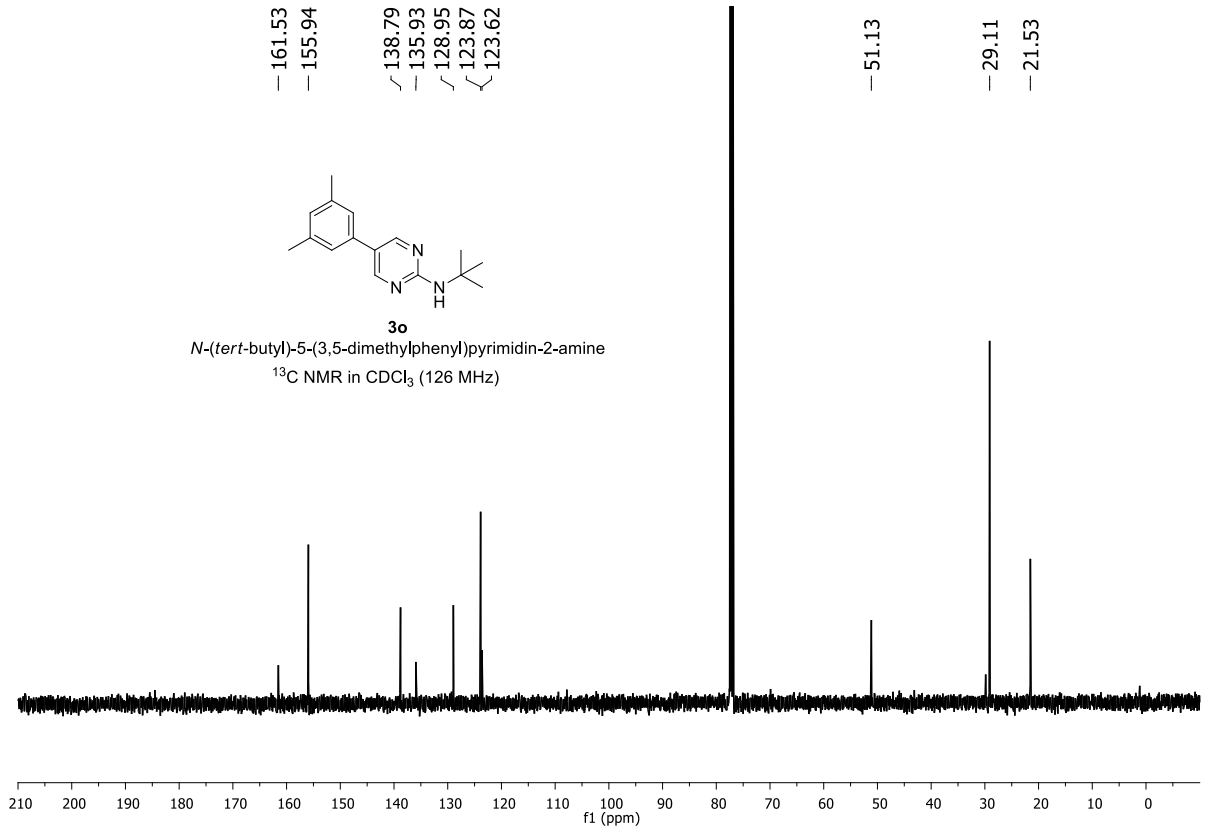
^{19}F NMR in $CDCl_3$ (417 MHz)



3o

N-(*tert*-butyl)-5-(3,5-dimethylphenyl)pyrimidin-2-amine

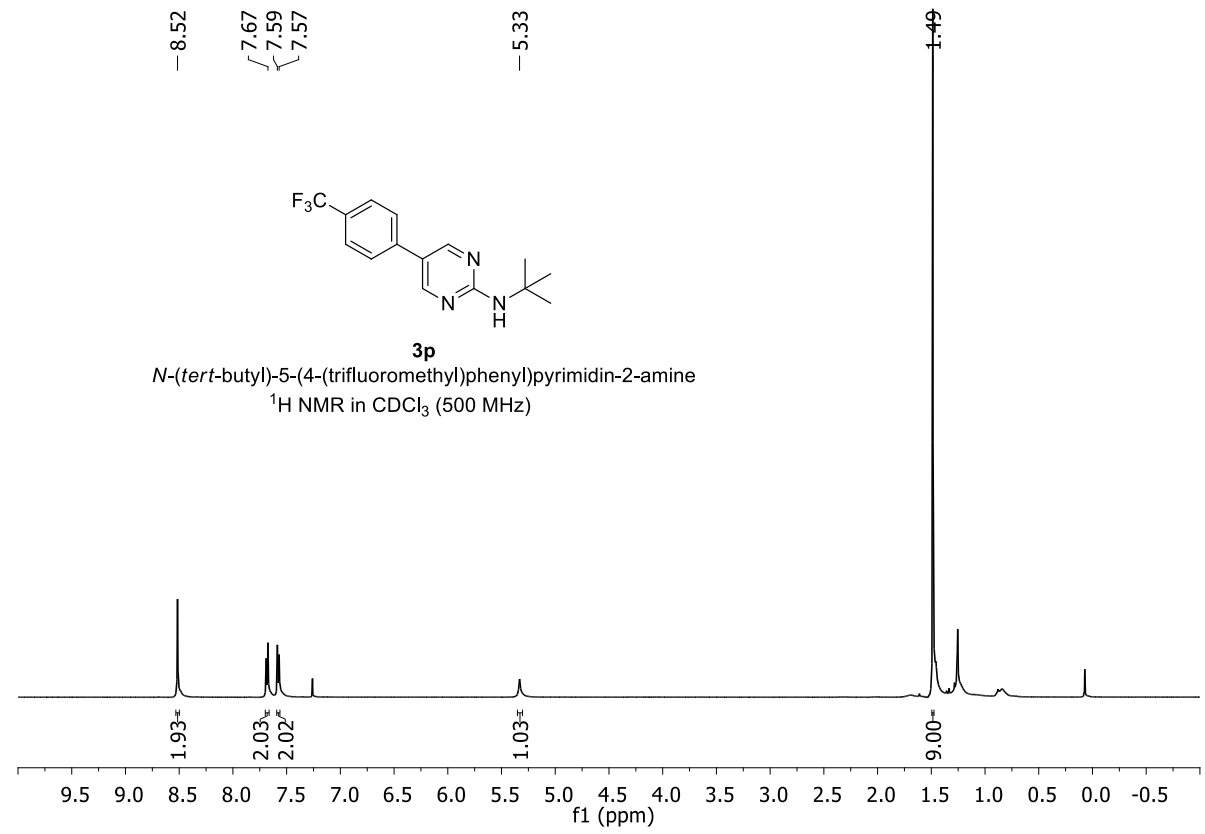
^{1}H NMR in $CDCl_3$ (400 MHz)



3o

N-(*tert*-butyl)-5-(3,5-dimethylphenyl)pyrimidin-2-amine

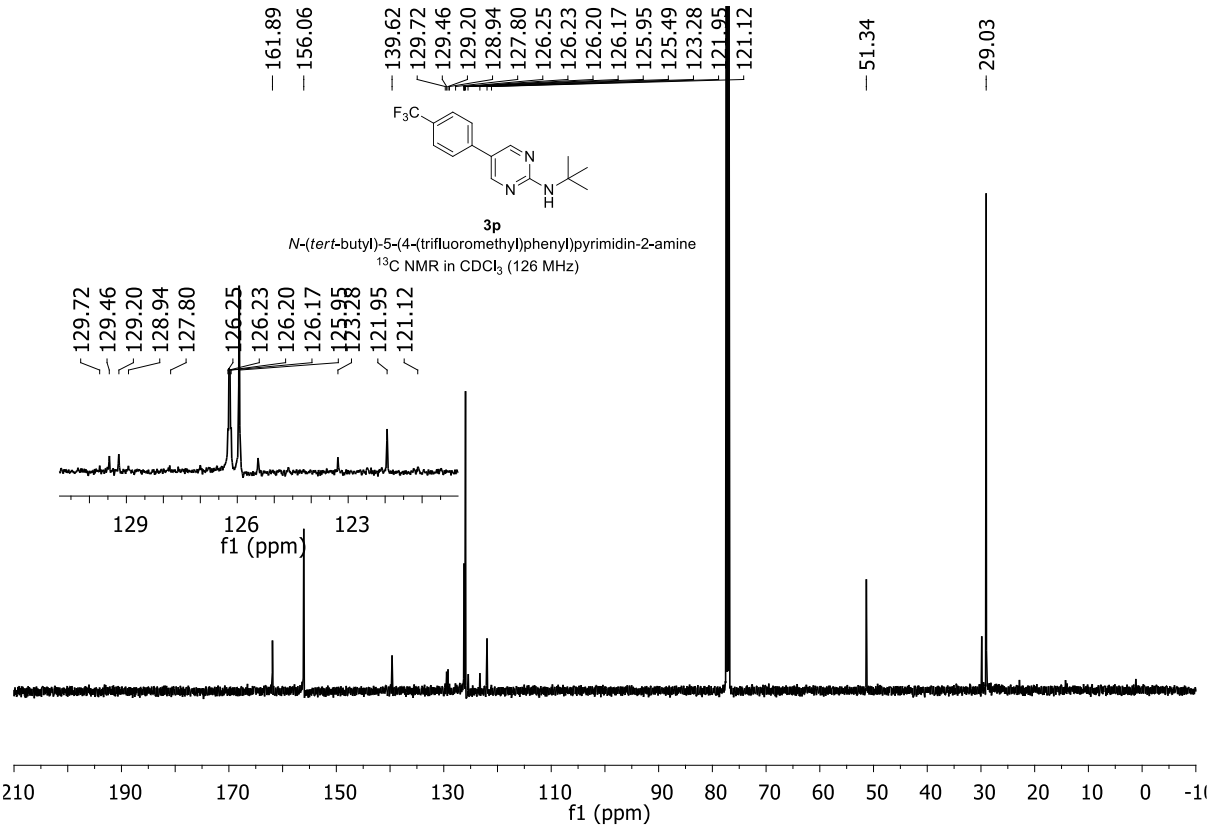
^{13}C NMR in $CDCl_3$ (126 MHz)



3p

N-(*tert*-butyl)-5-(4-(trifluoromethyl)phenyl)pyrimidin-2-amine

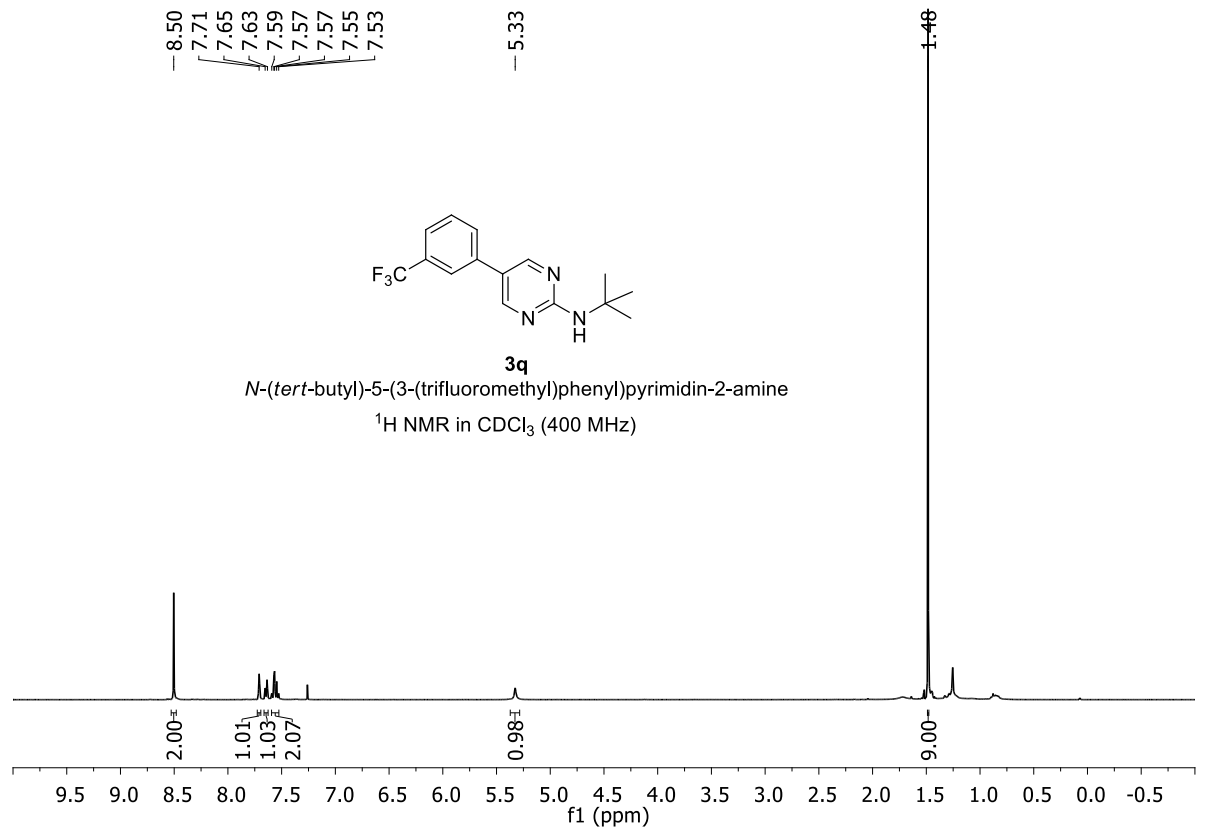
^{1}H NMR in $CDCl_3$ (500 MHz)



3p

N-(*tert*-butyl)-5-(4-(trifluoromethyl)phenyl)pyrimidin-2-amine

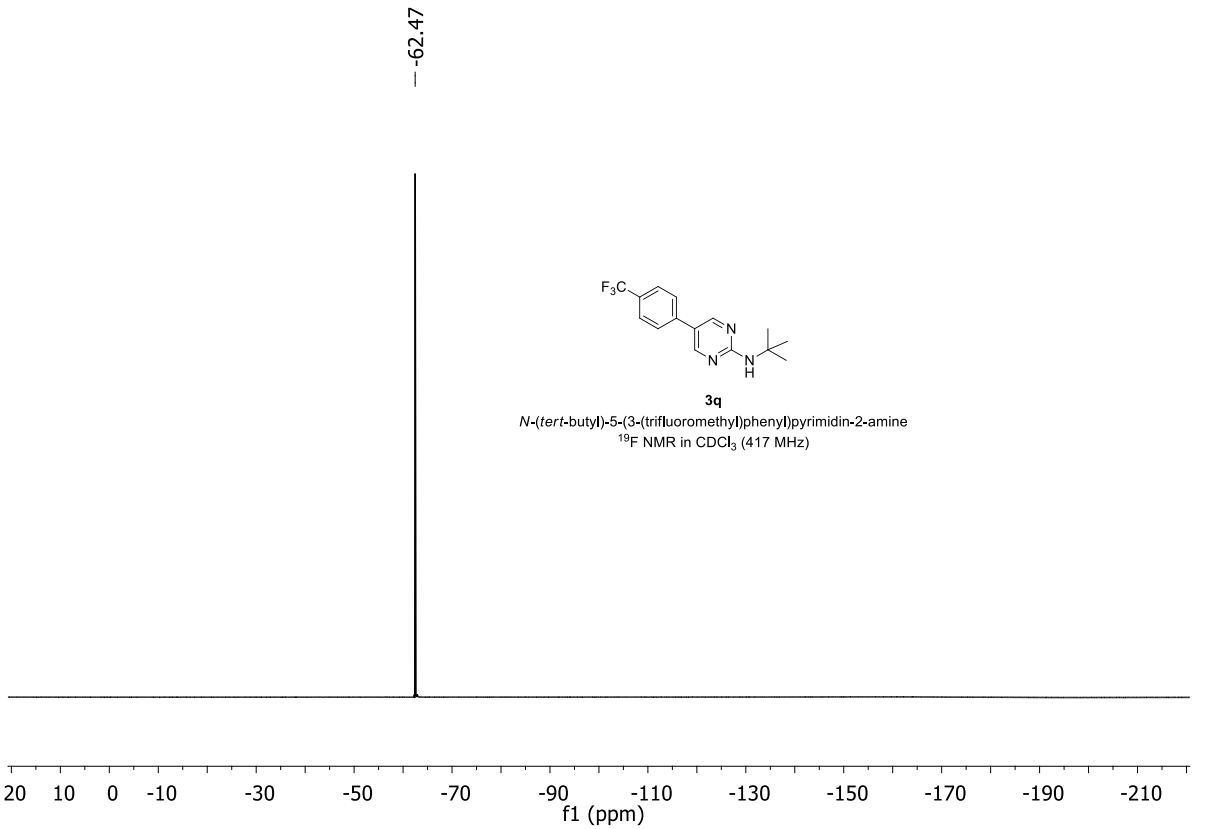
^{13}C NMR in $CDCl_3$ (126 MHz)

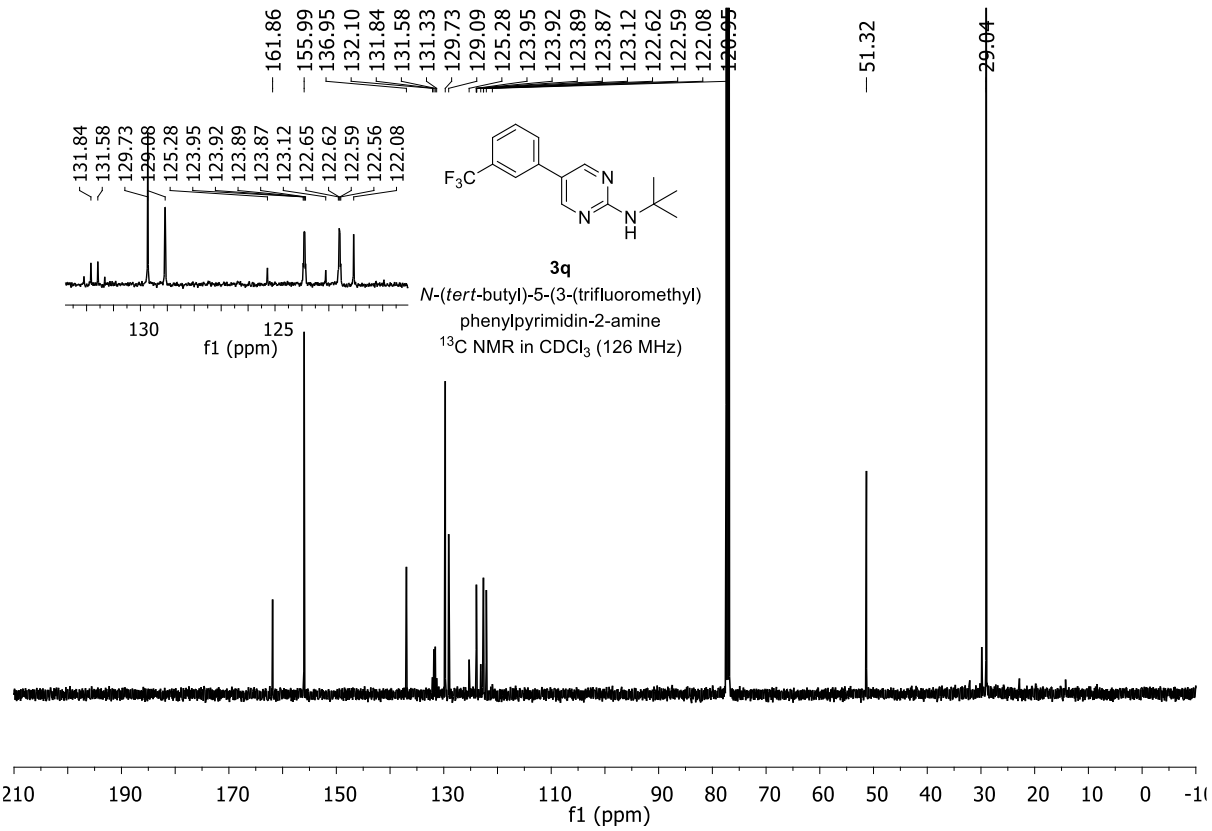


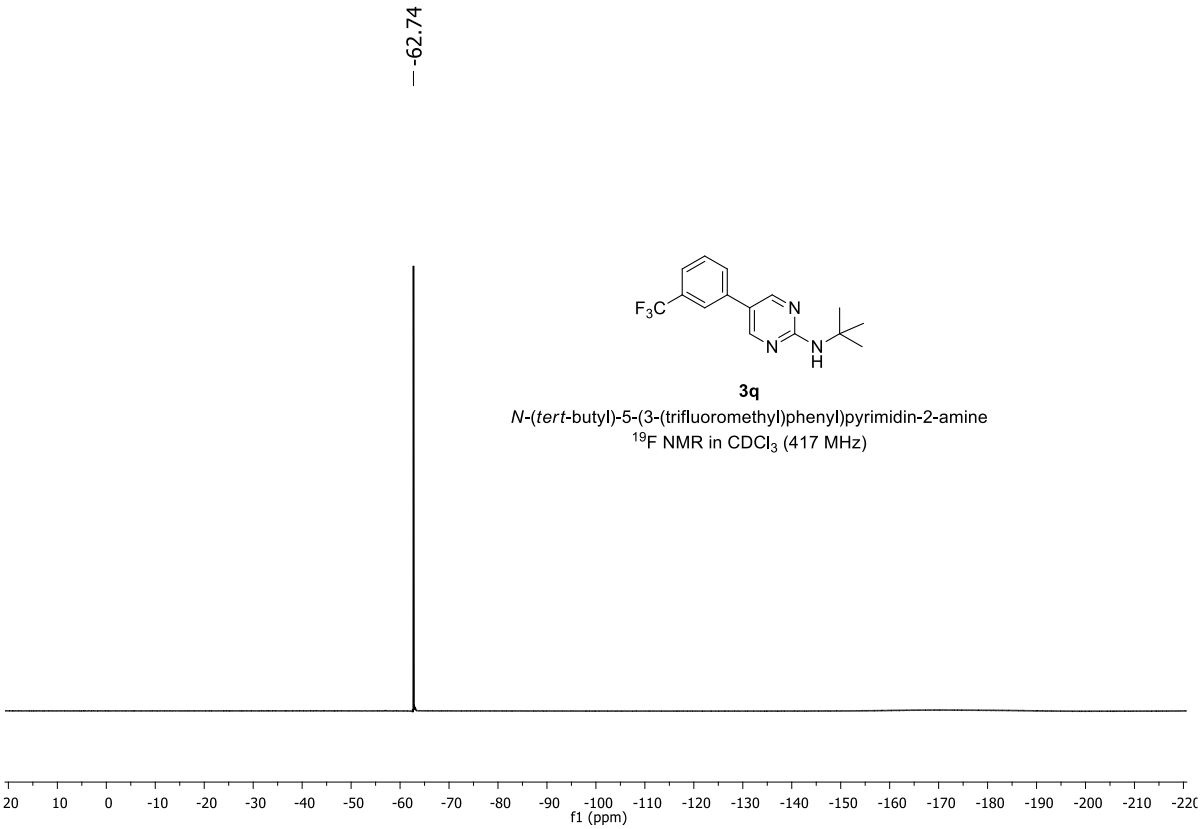
3q

N-(*tert*-butyl)-5-(3-(trifluoromethyl)phenyl)pyrimidin-2-amine

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


-62.47
F3C
N
N
N
H
3q
N-(tert-butyl)-5-(3-(trifluoromethyl)phenyl)pyrimidin-2-amine
19F NMR in CDCl3 (417 MHz)
20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

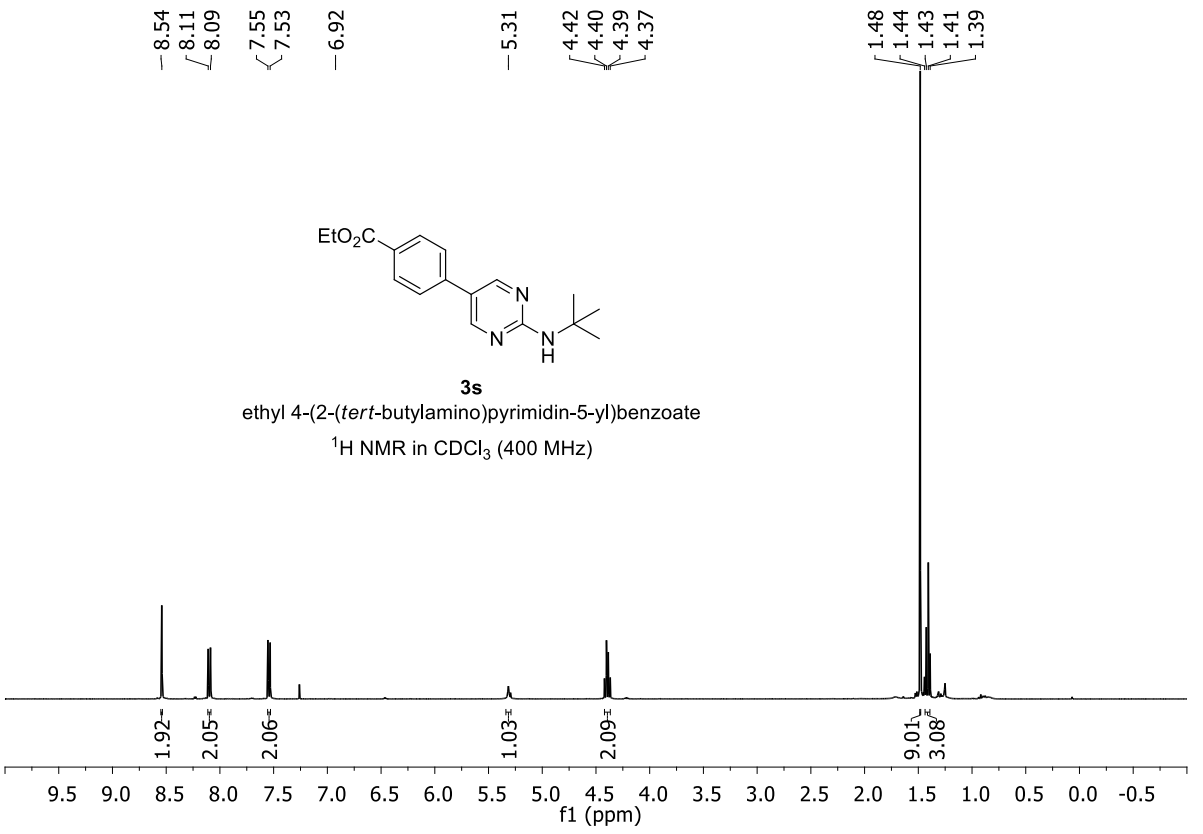

161.86
155.99
136.95
132.10
131.84
131.58
131.33
129.73
129.09
125.28
123.95
123.92
123.89
123.87
123.12
122.62
122.59
122.08
120.95
51.32
29.04
131.84
131.58
129.73
129.08
125.28
123.95
123.92
123.89
123.87
123.12
122.65
122.62
122.59
122.56
122.08
130
125
f1 (ppm)
F3C
N
N
N
H
3q
N-(tert-butyl)-5-(3-(trifluoromethyl)
phenylpyrimidin-2-amine
13C NMR in CDCl3 (126 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3q

N-(*tert*-butyl)-5-(3-(trifluoromethyl)phenyl)pyrimidin-2-amine

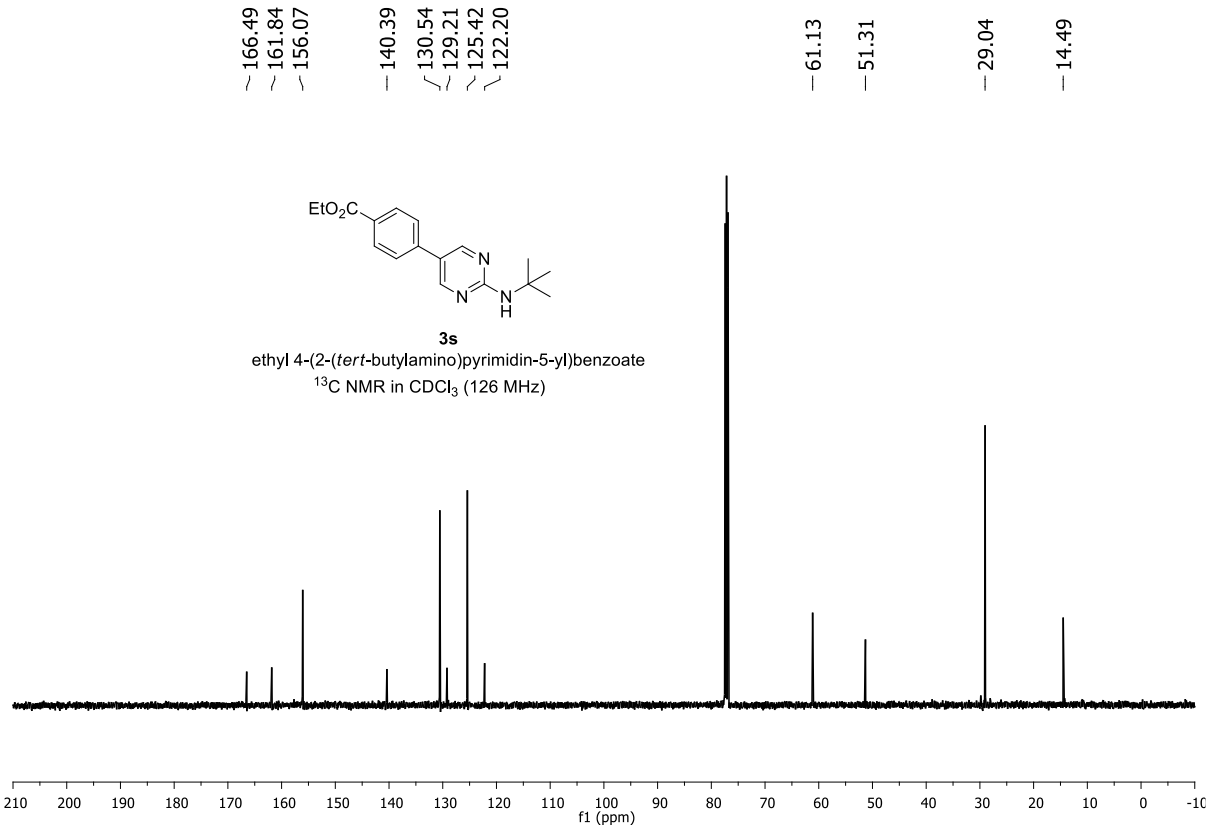
^{19}F NMR in $CDCl_3$ (417 MHz)



3s

ethyl 4-(2-(*tert*-butylamino)pyrimidin-5-yl)benzoate

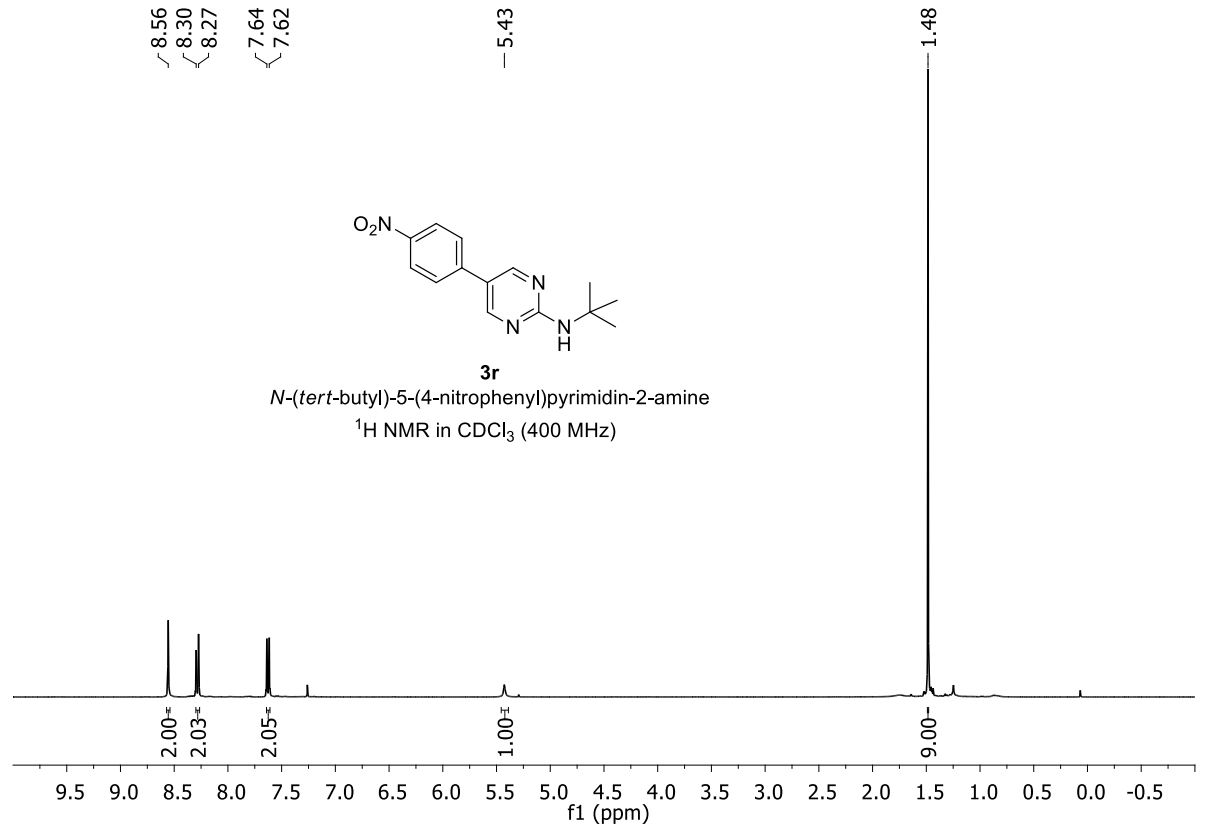
^{1}H NMR in $CDCl_3$ (400 MHz)



3s

ethyl 4-(2-(*tert*-butylamino)pyrimidin-5-yl)benzoate

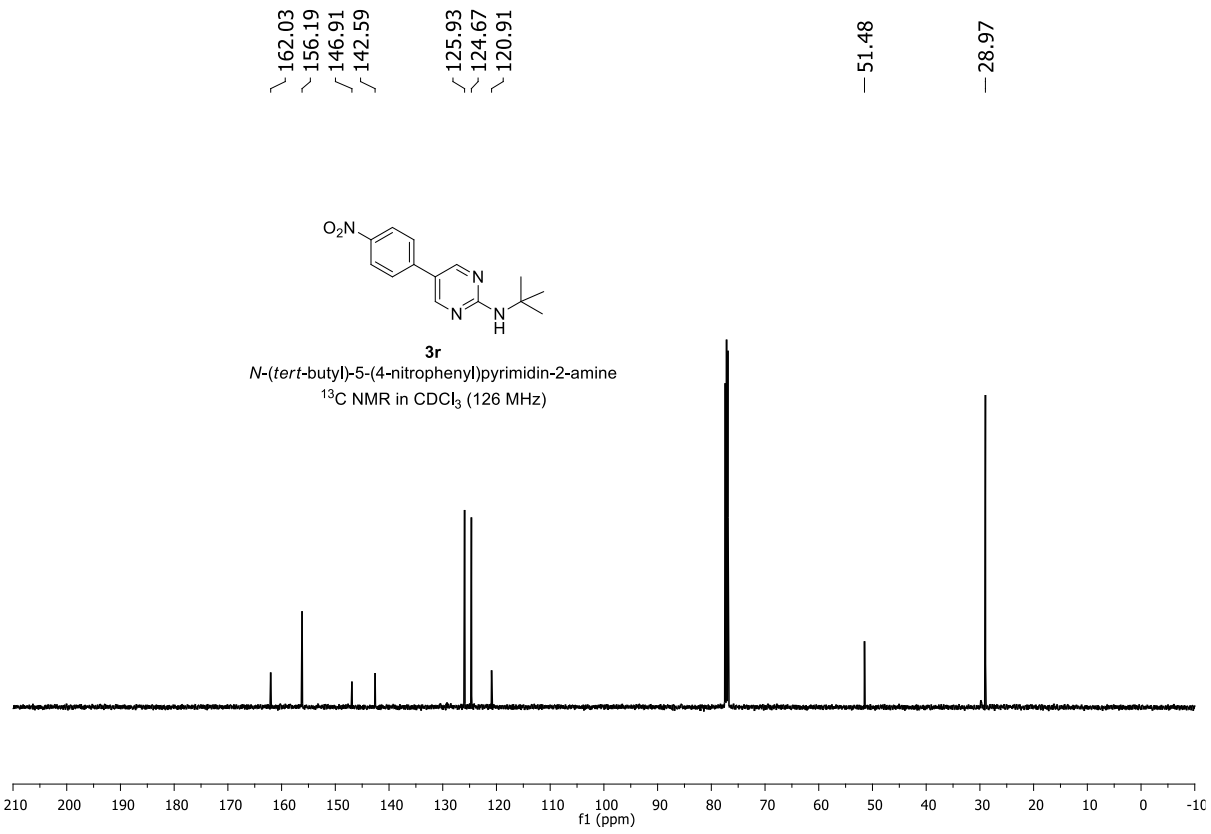
^{13}C NMR in $CDCl_3$ (126 MHz)



3r

N-(*tert*-butyl)-5-(4-nitrophenyl)pyrimidin-2-amine

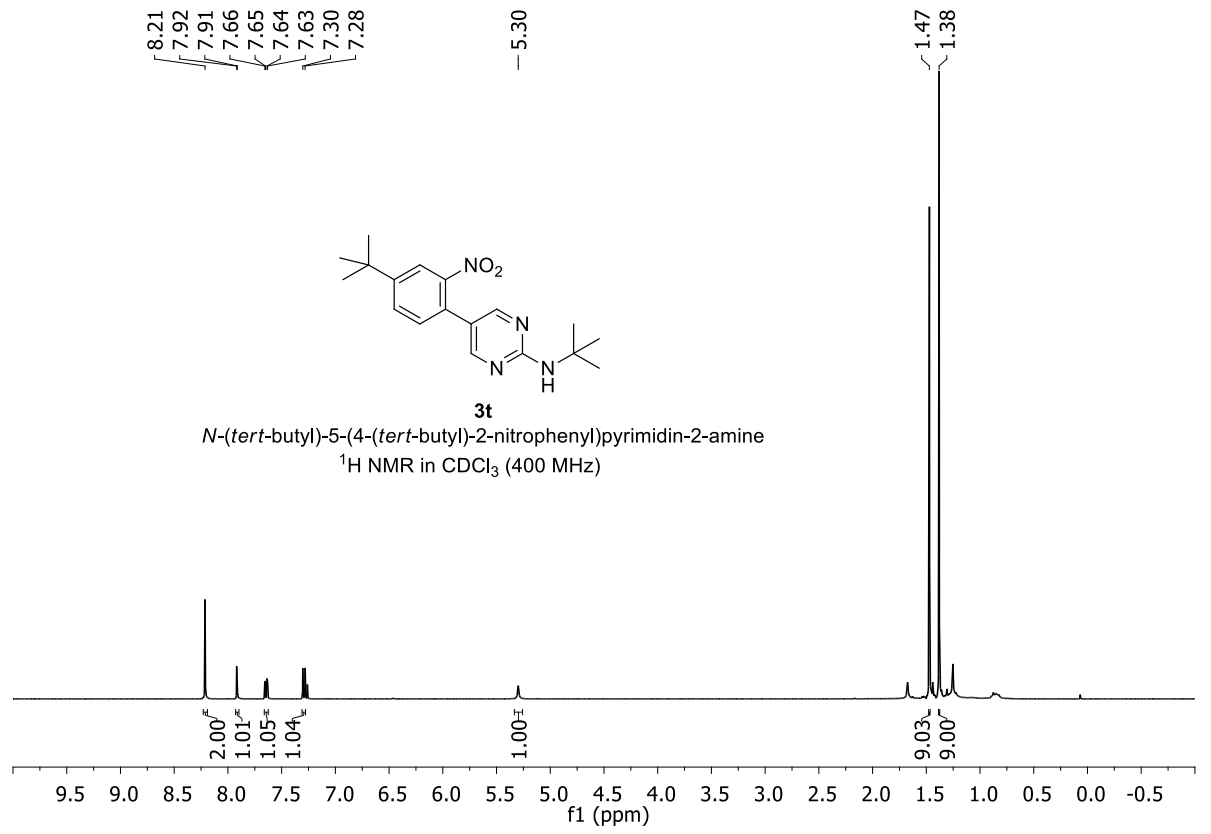
^{1}H NMR in $CDCl_3$ (400 MHz)



3r

N-(*tert*-butyl)-5-(4-nitrophenyl)pyrimidin-2-amine

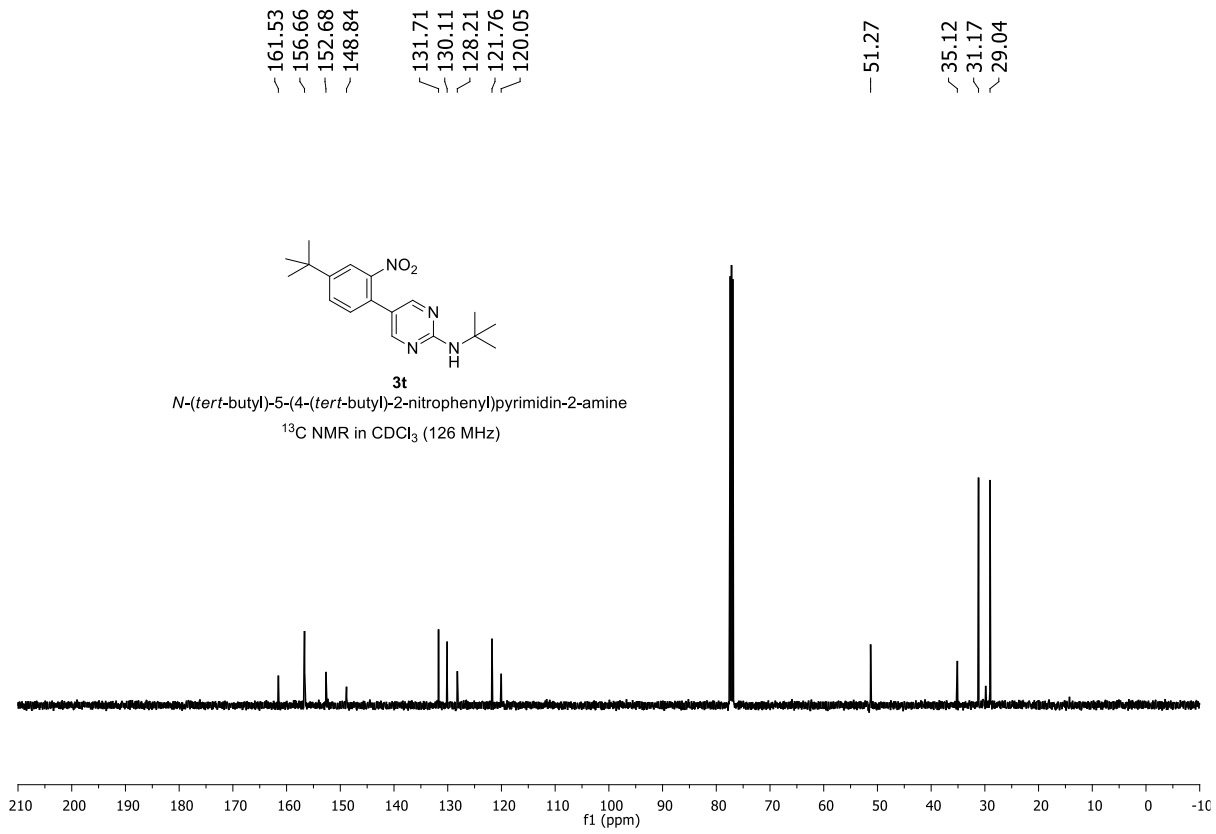
^{13}C NMR in $CDCl_3$ (126 MHz)



3t

N-(*tert*-butyl)-5-(4-(*tert*-butyl)-2-nitrophenyl)pyrimidin-2-amine

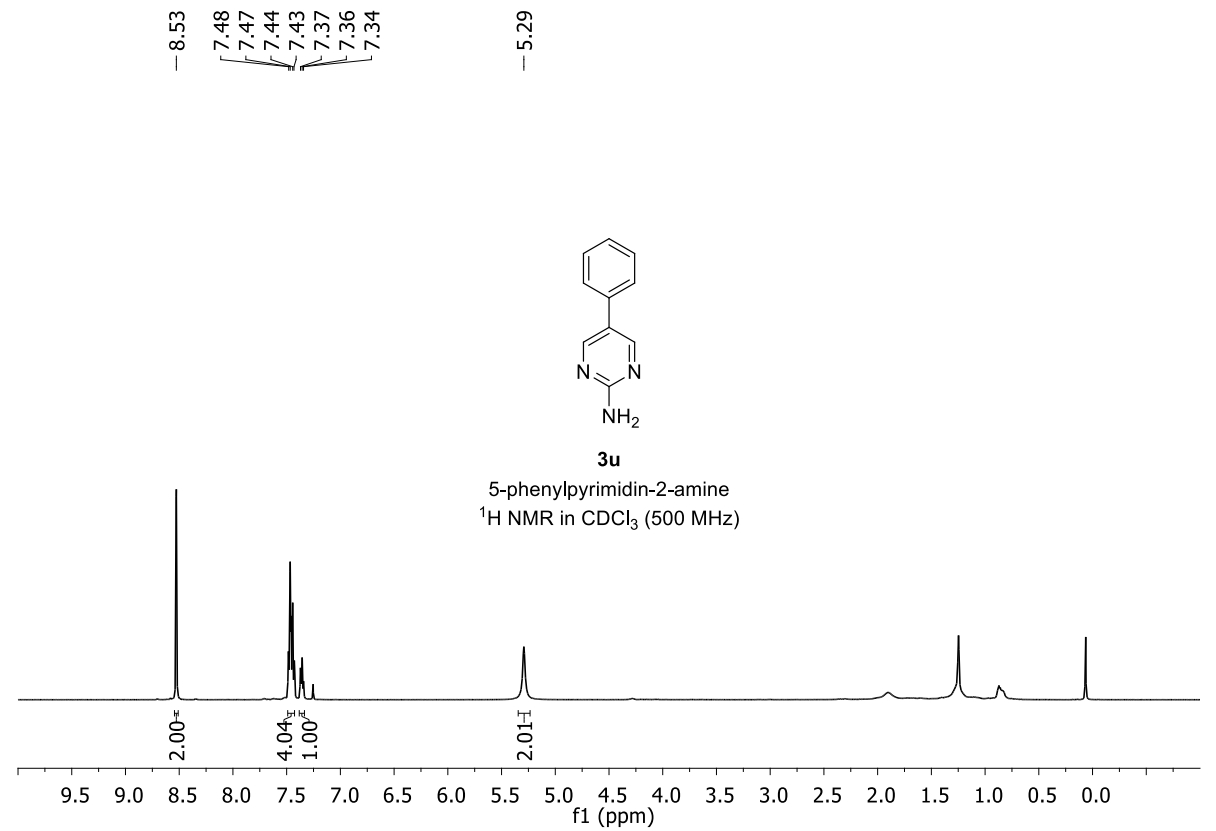
^{1}H NMR in $CDCl_3$ (400 MHz)



3t

N-(*tert*-butyl)-5-(4-(*tert*-butyl)-2-nitrophenyl)pyrimidin-2-amine

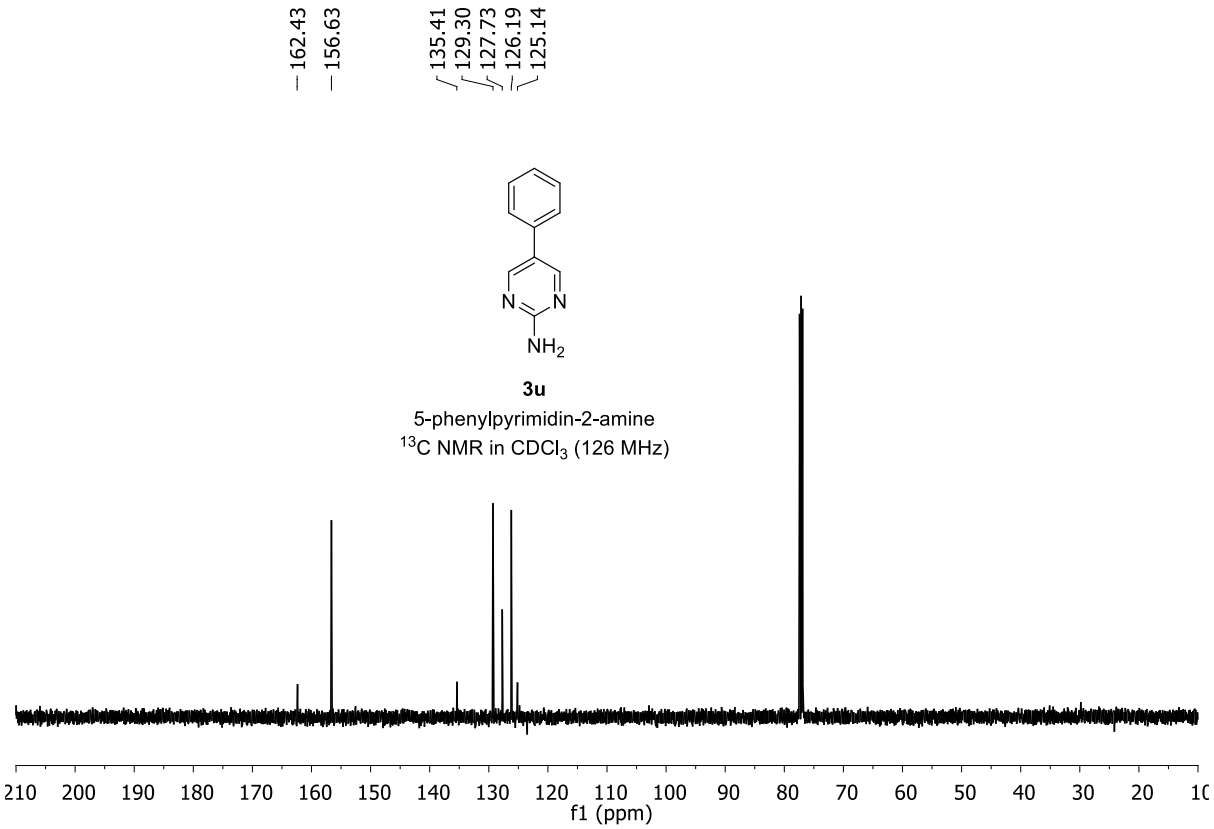
^{13}C NMR in $CDCl_3$ (126 MHz)



3u

5-phenylpyrimidin-2-amine

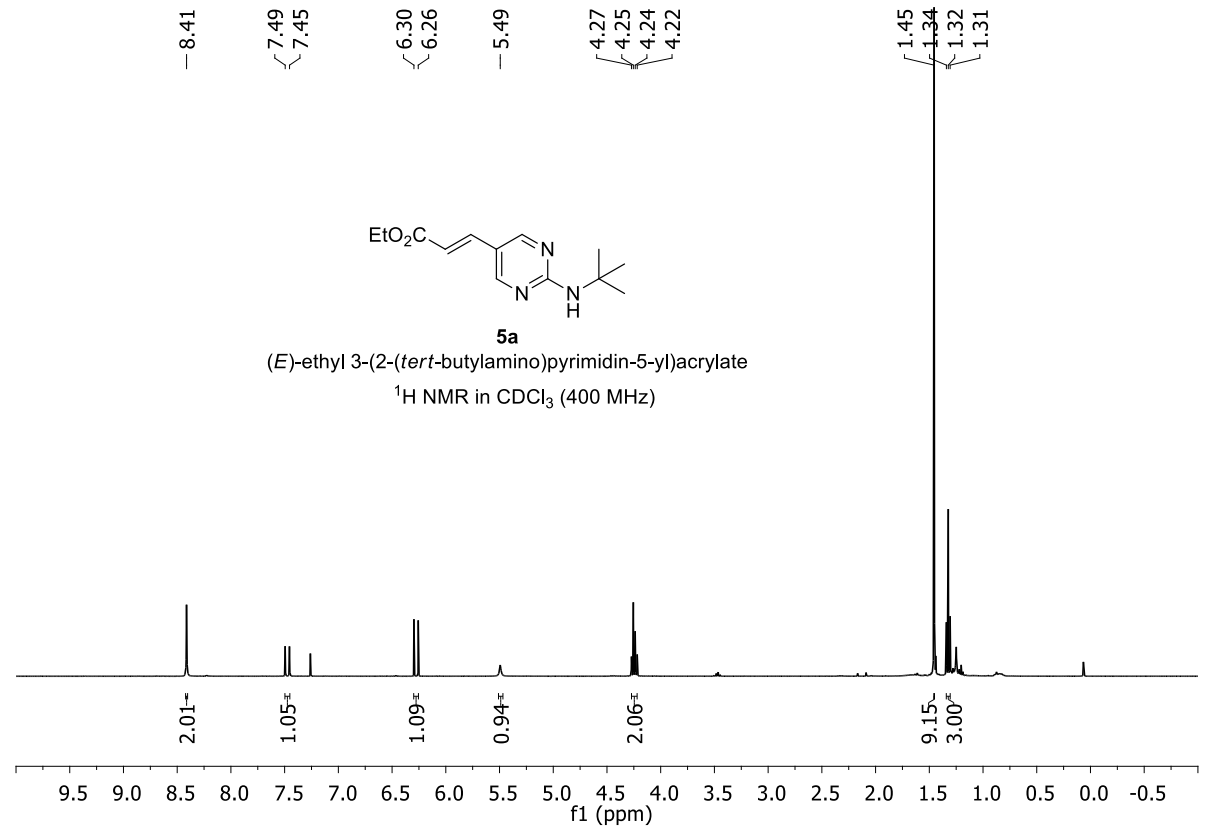
^{1}H NMR in $CDCl_3$ (500 MHz)



3u

5-phenylpyrimidin-2-amine

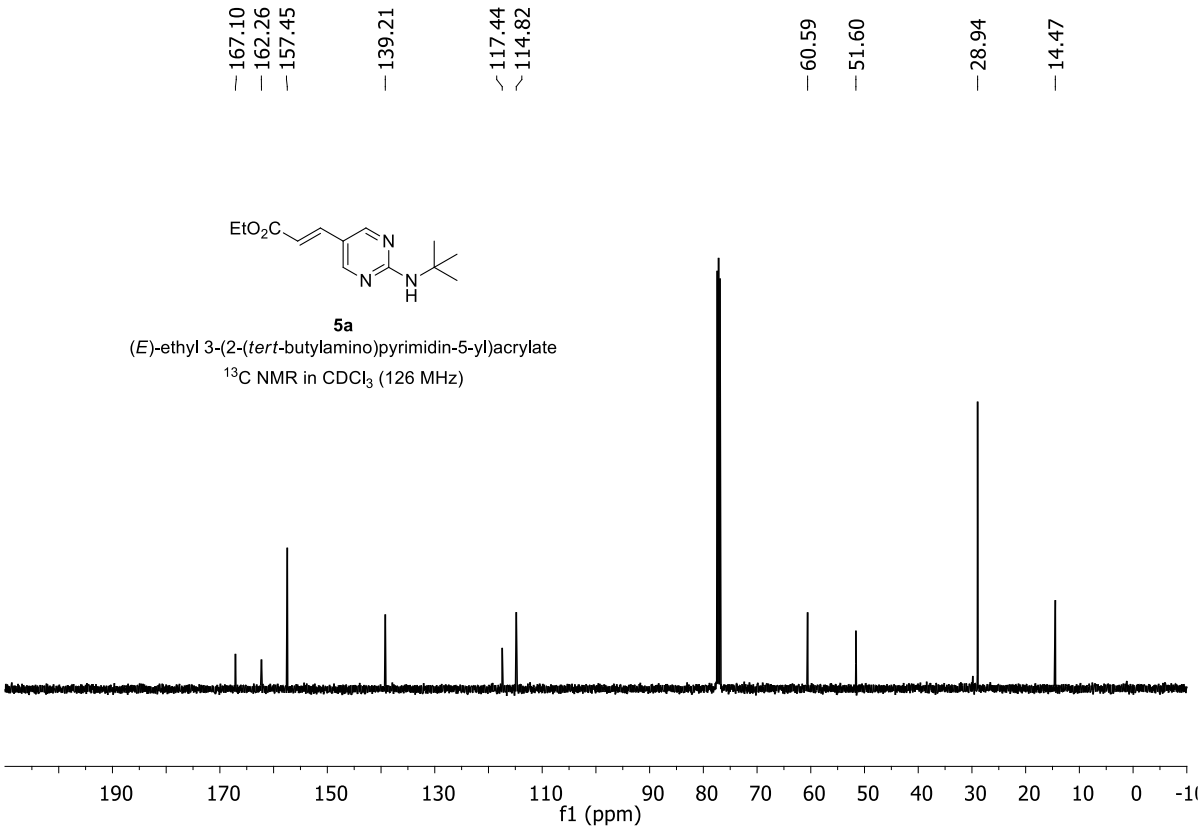
^{13}C NMR in $CDCl_3$ (126 MHz)



5a

(*E*)-ethyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate

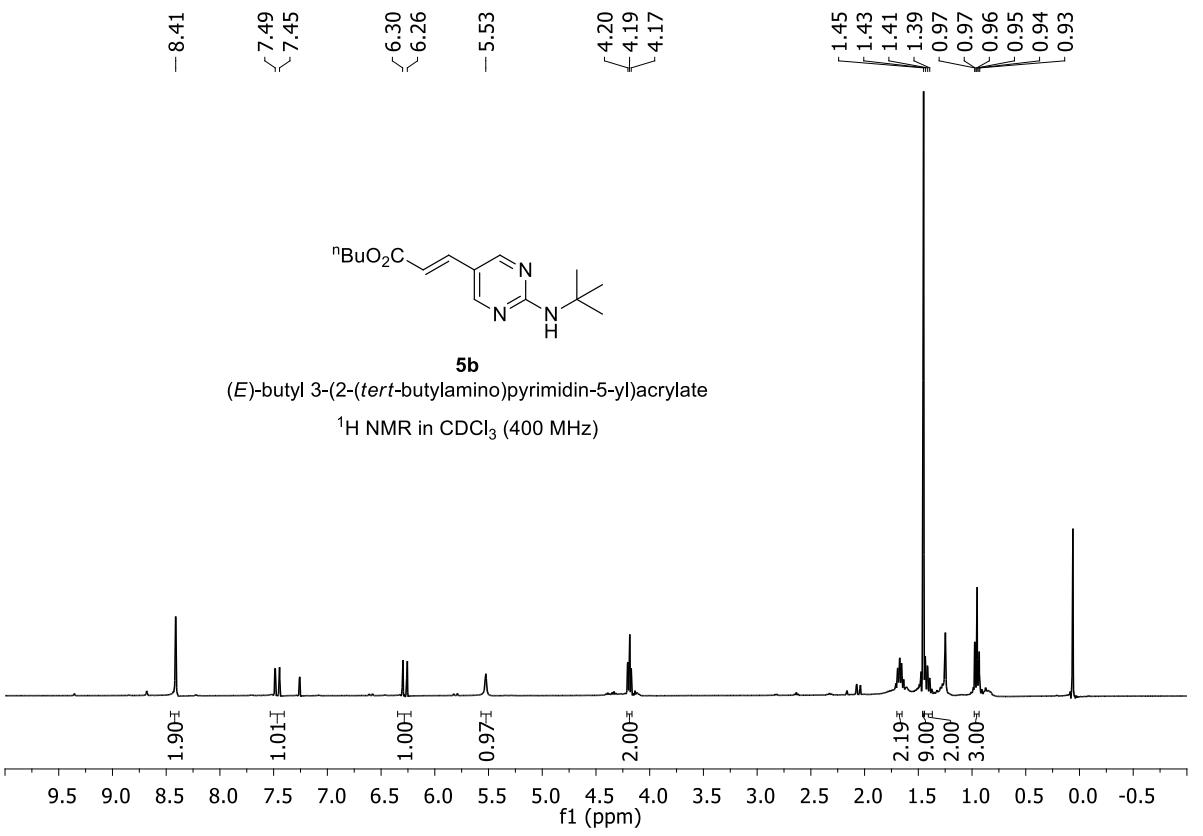
^{1}H NMR in $CDCl_3$ (400 MHz)



5a

(*E*)-ethyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate

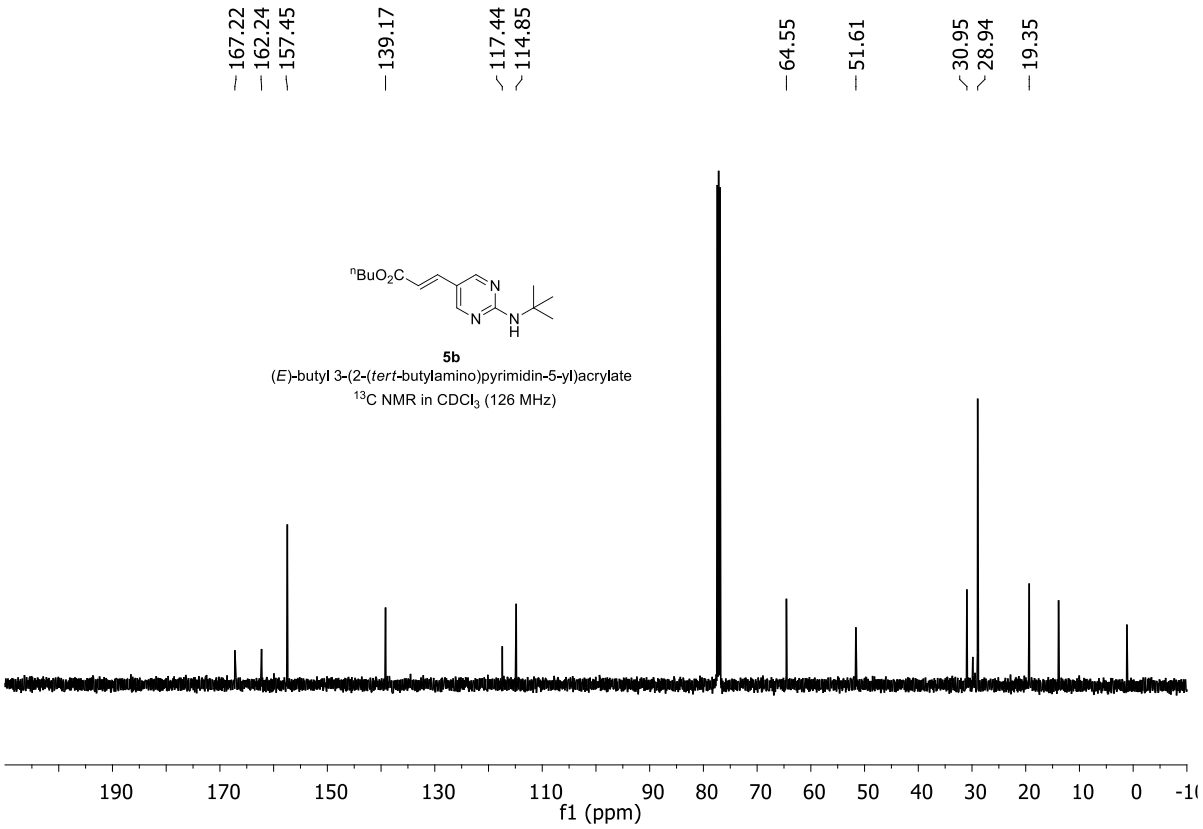
^{13}C NMR in $CDCl_3$ (126 MHz)



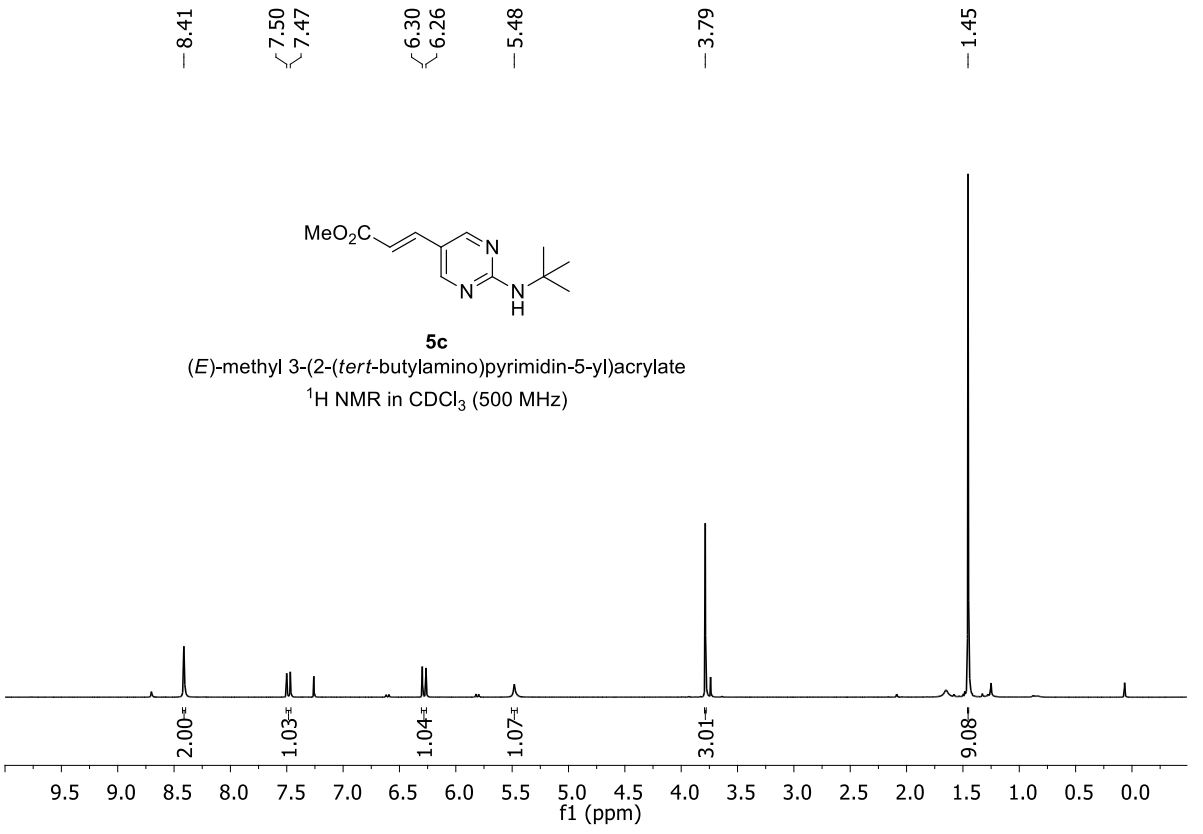
5b

(*E*)-butyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate

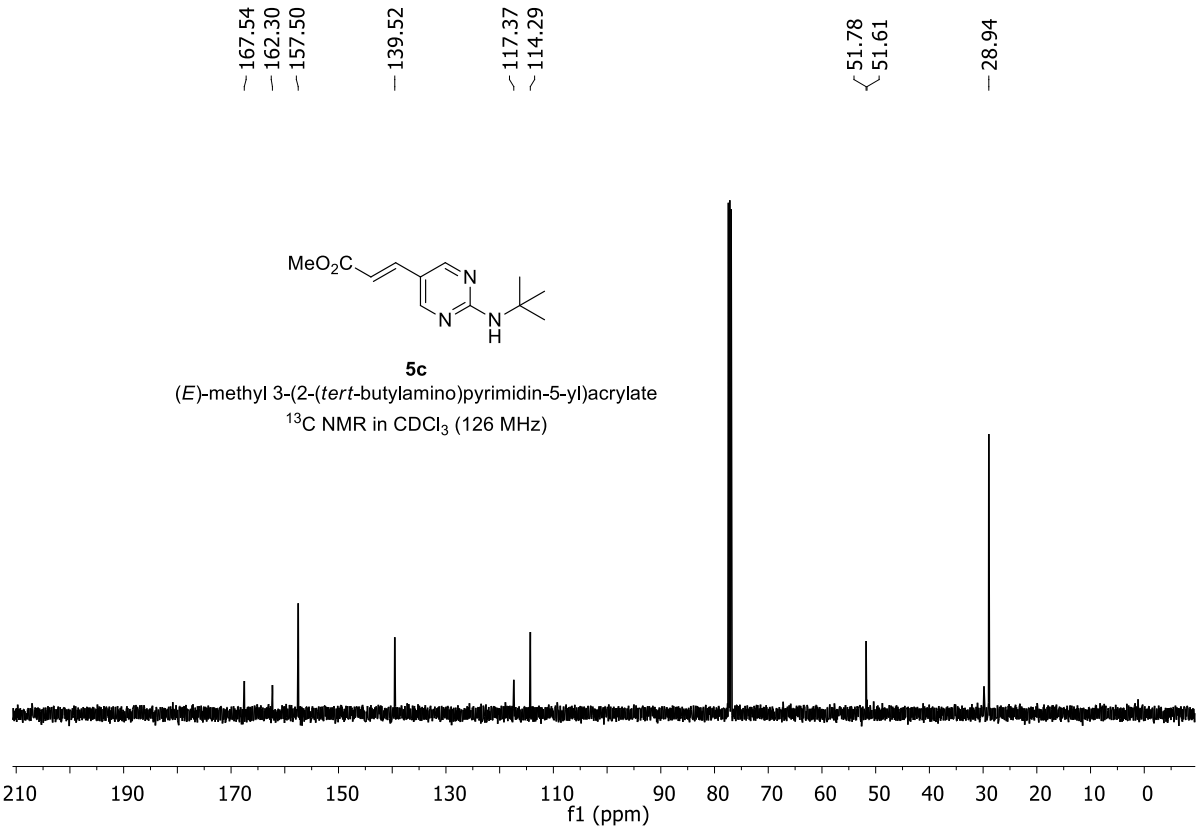
^{1}H NMR in $CDCl_3$ (400 MHz)



5b
(*E*)-butyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (126 MHz)



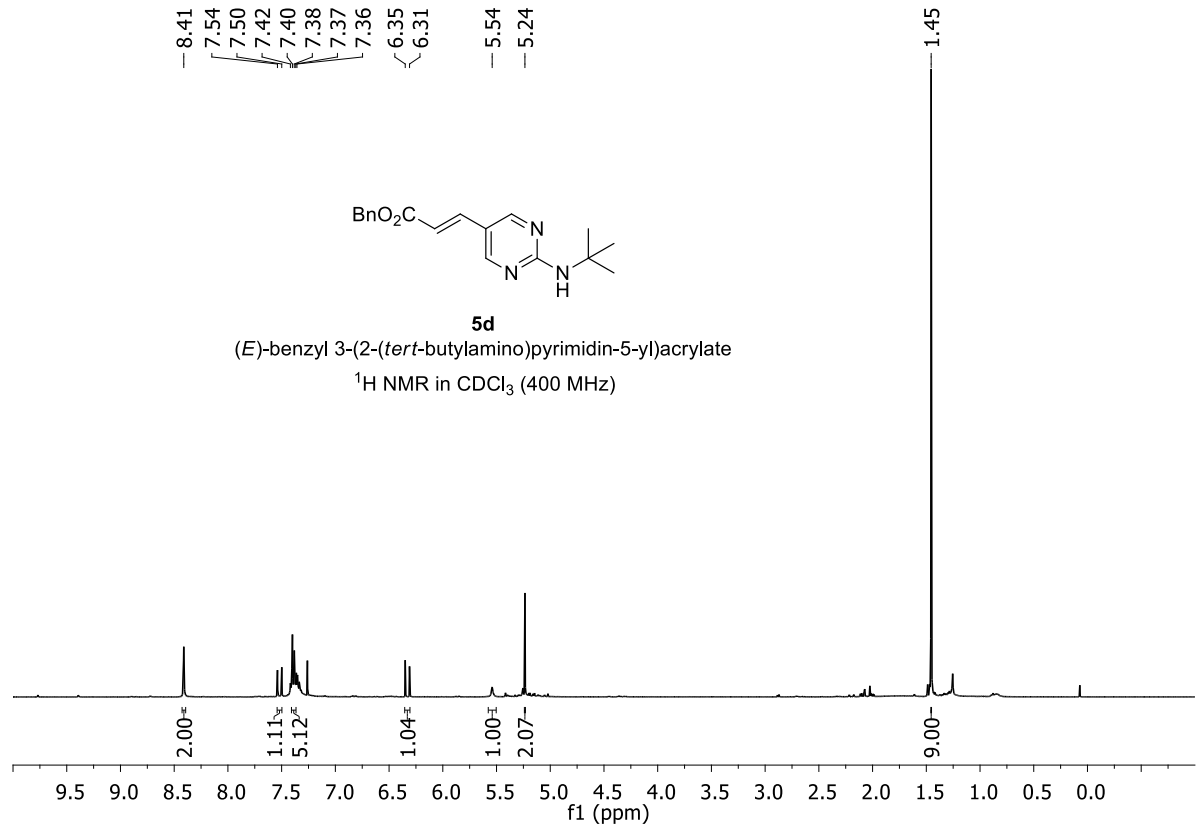
5c
(*E*)-methyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (500 MHz)



5c

(*E*)-methyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate

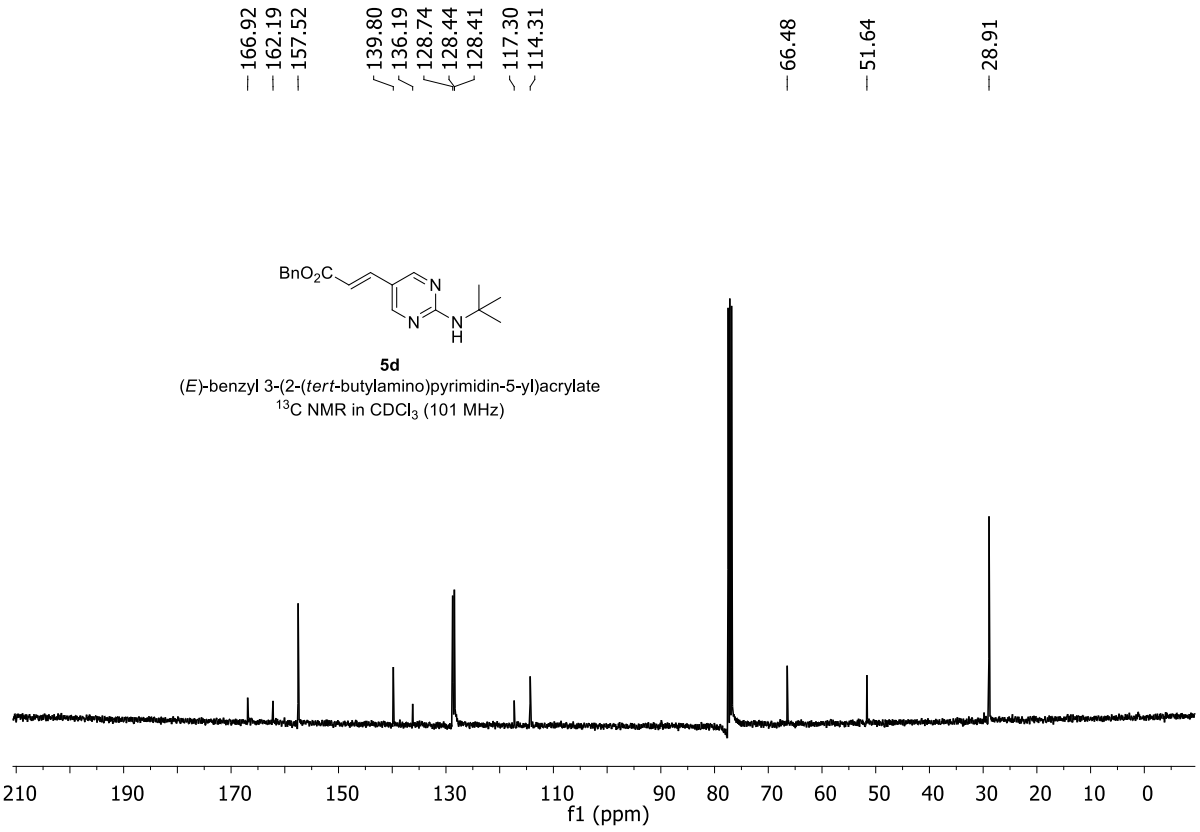
^{13}C NMR in $CDCl_3$ (126 MHz)



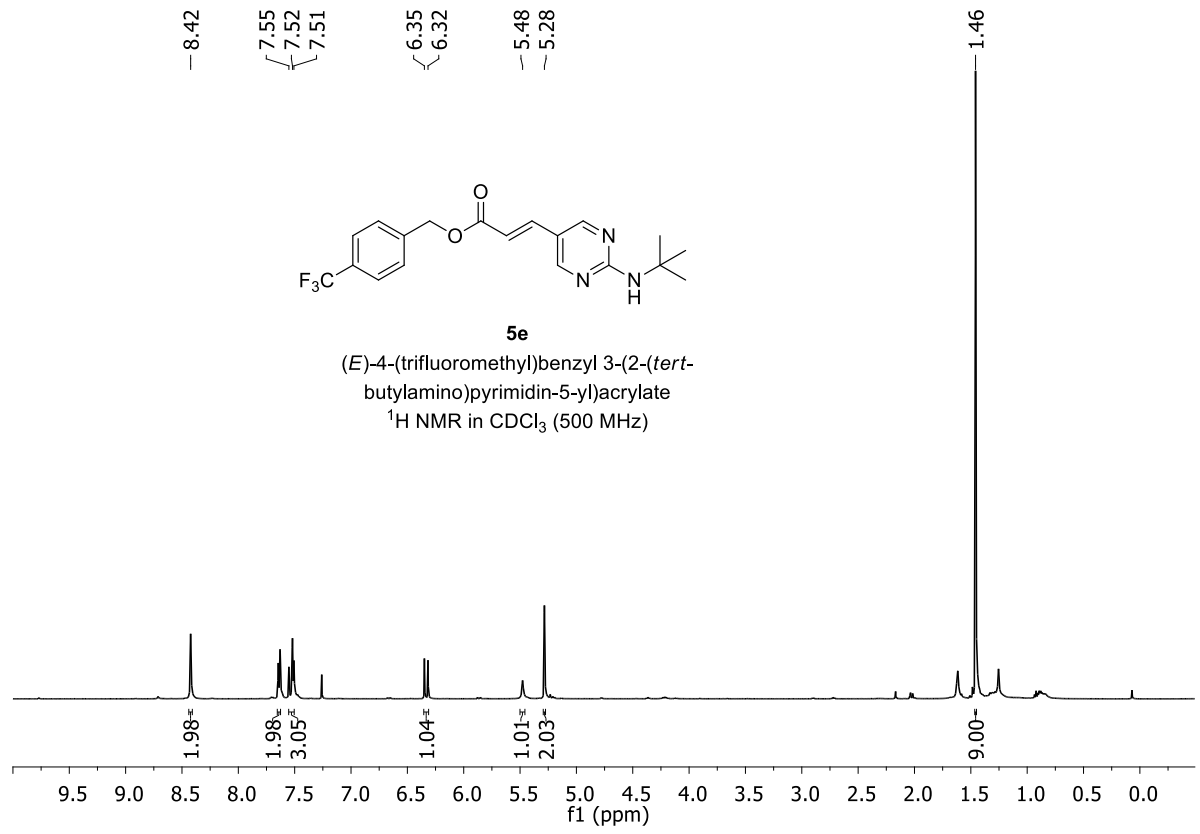
5d

(*E*)-benzyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate

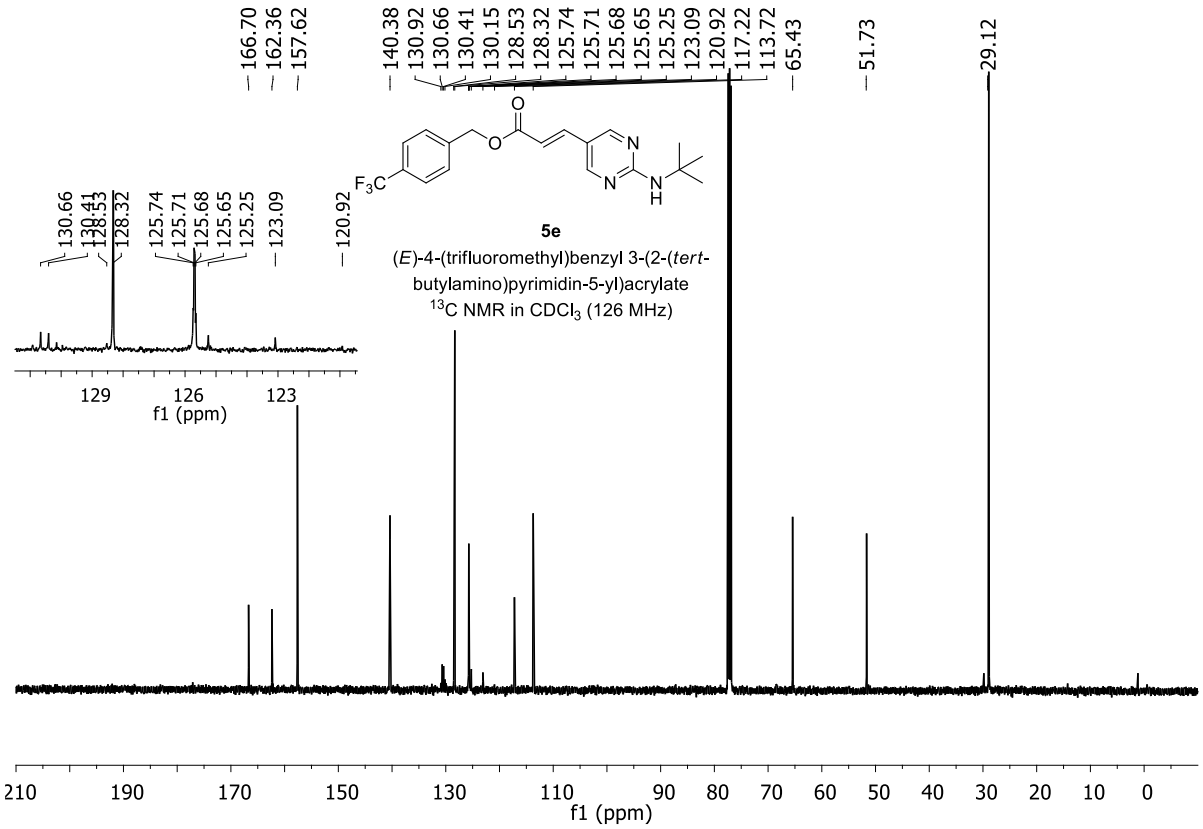
^{1}H NMR in $CDCl_3$ (400 MHz)



5d
(*E*)-benzyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (101 MHz)



5e
(*E*)-4-(trifluoromethyl)benzyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (500 MHz)


166.70
162.36
157.62
140.38
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130.66
130.41
130.15
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128.32
125.74
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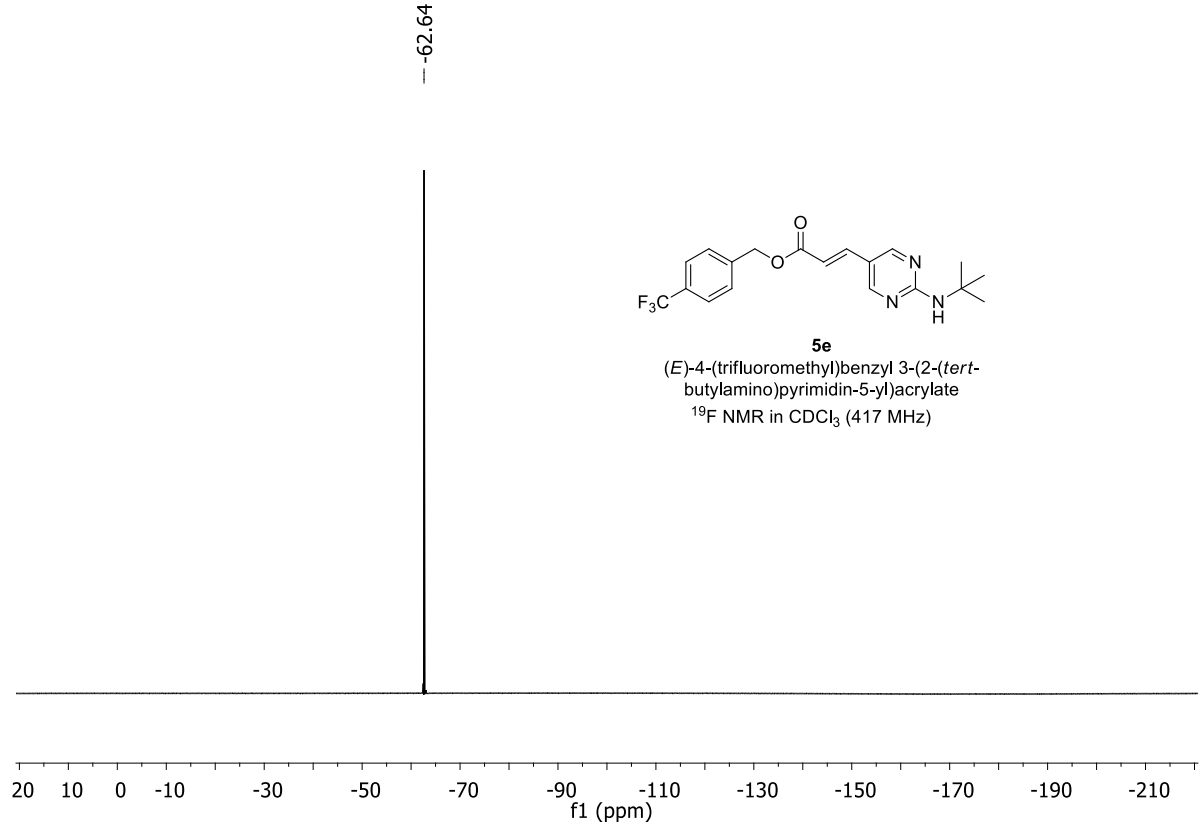
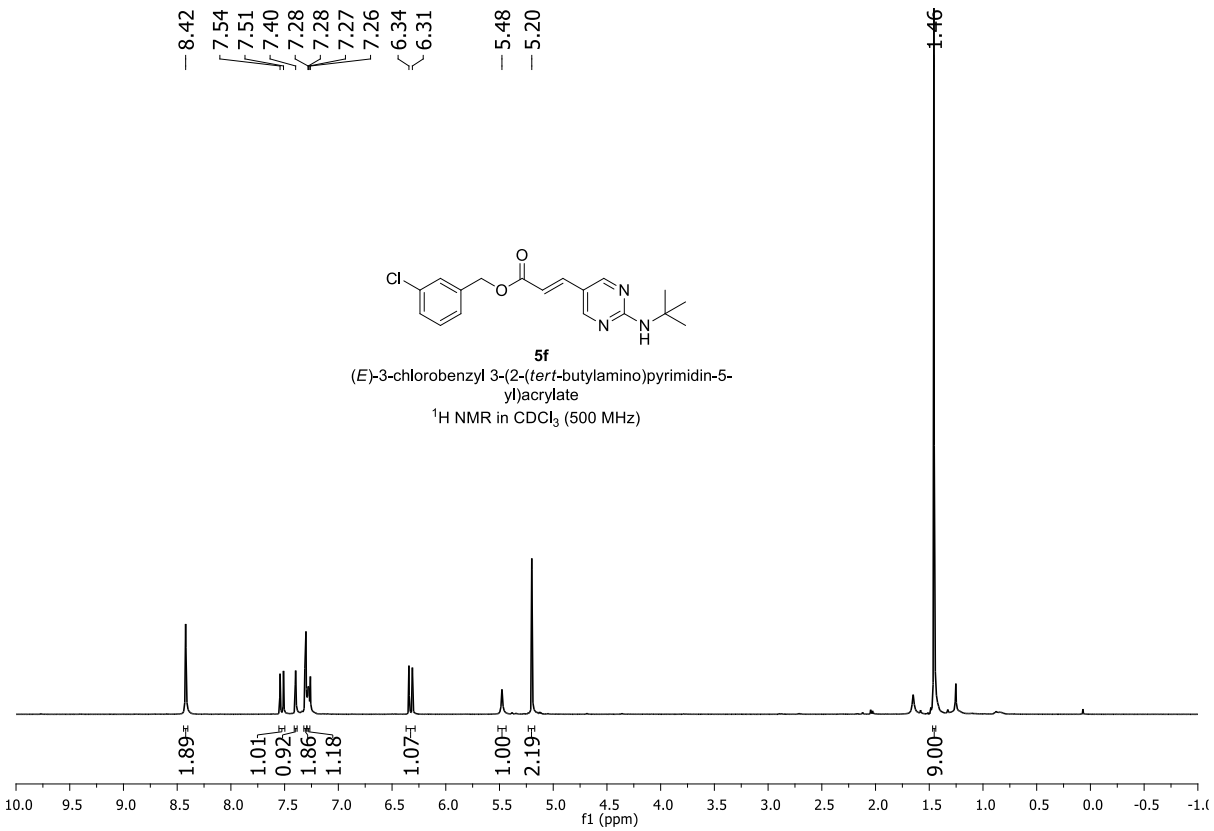
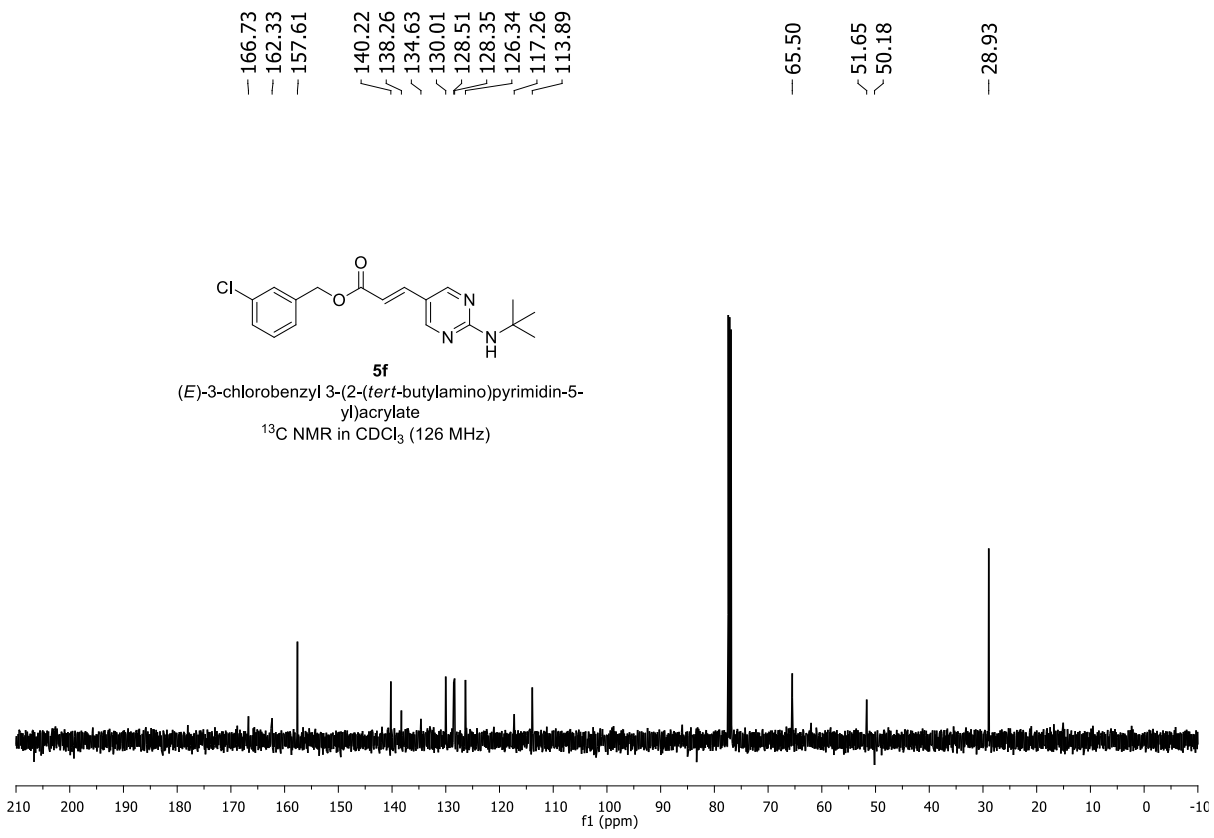
125.65
125.25
123.09
120.92
117.22
113.72
65.43
51.73
29.12
F3C
O
N
H
5e
(E)-4-(trifluoromethyl)benzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate
13C NMR in CDCl3 (126 MHz)
f1 (ppm)

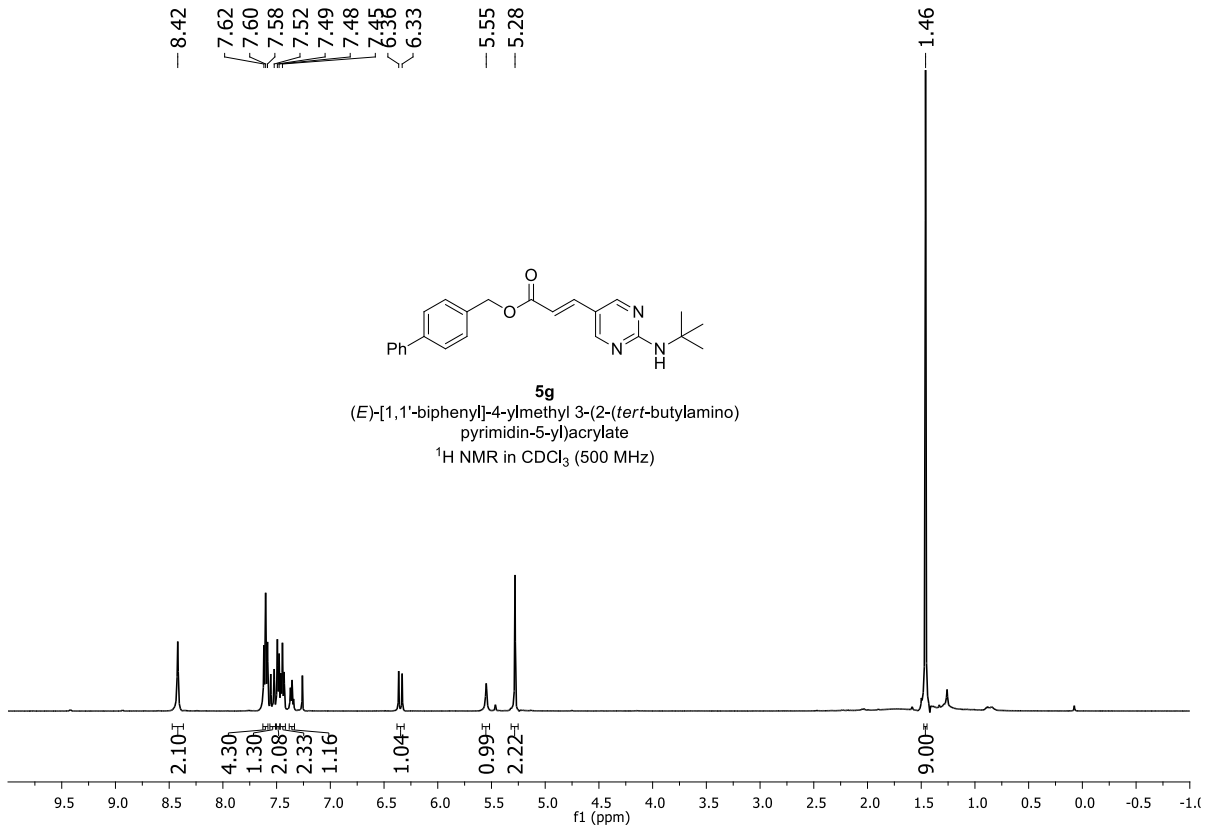

-62.64
F3C
O
N
H
5e
(E)-4-(trifluoromethyl)benzyl 3-(2-(tert-butylamino)pyrimidin-5-yl)acrylate
19F NMR in CDCl3 (417 MHz)
f1 (ppm)



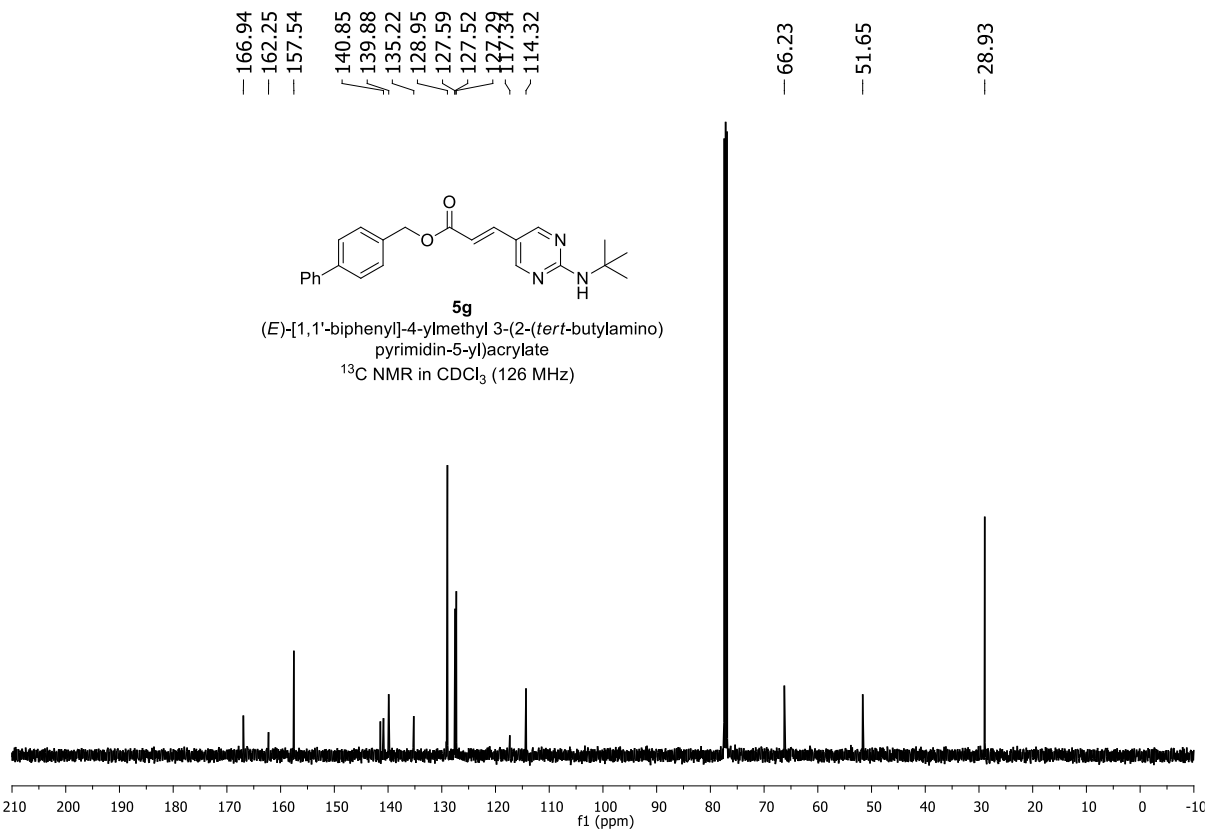
5f
(*E*)-3-chlorobenzyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (500 MHz)



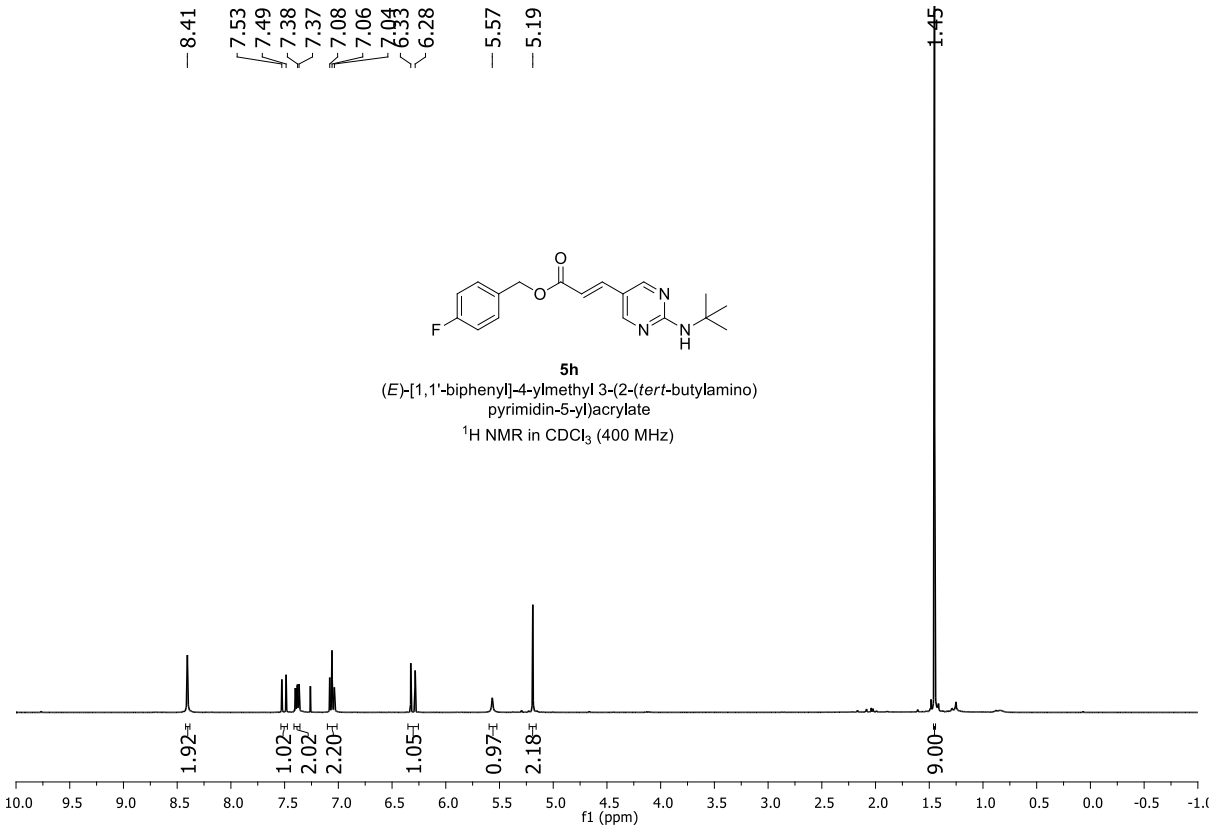
5f
(*E*)-3-chlorobenzyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (126 MHz)



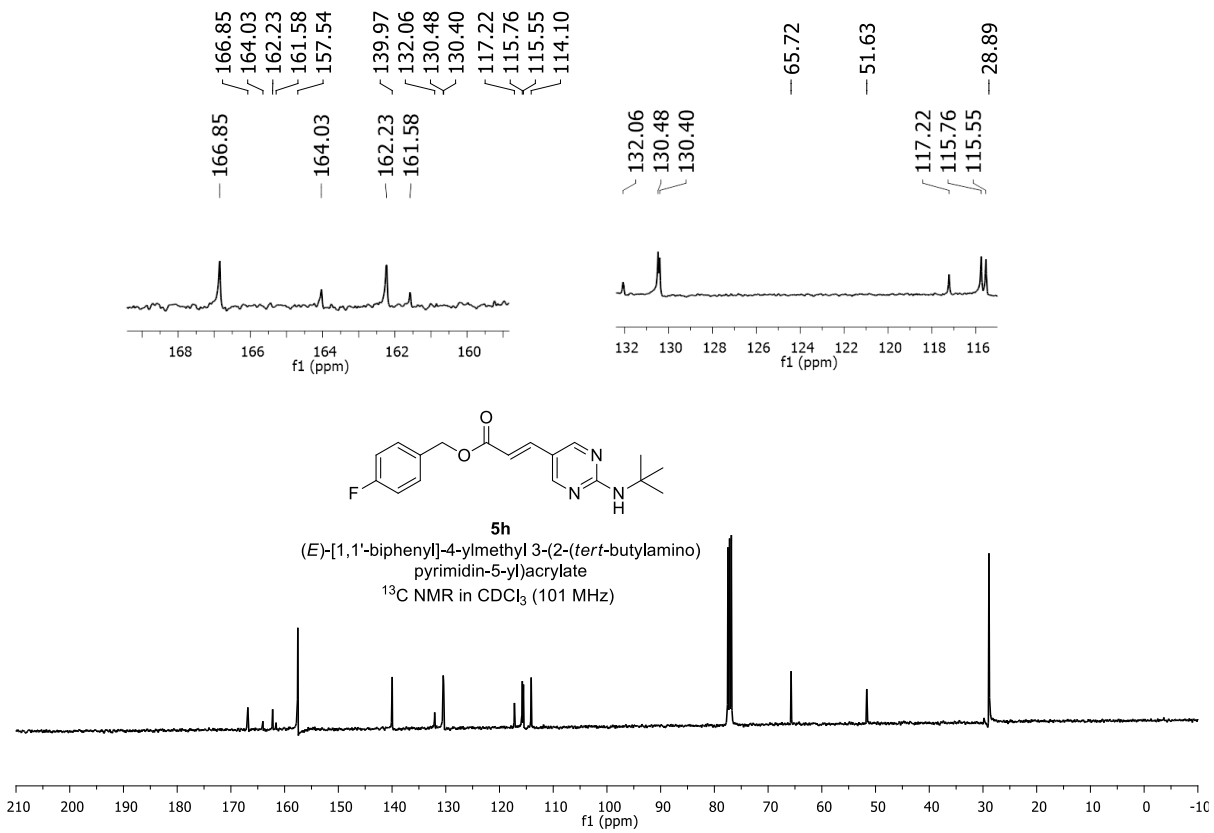
5g
(*E*)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(*tert*-butylamino) pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (500 MHz)



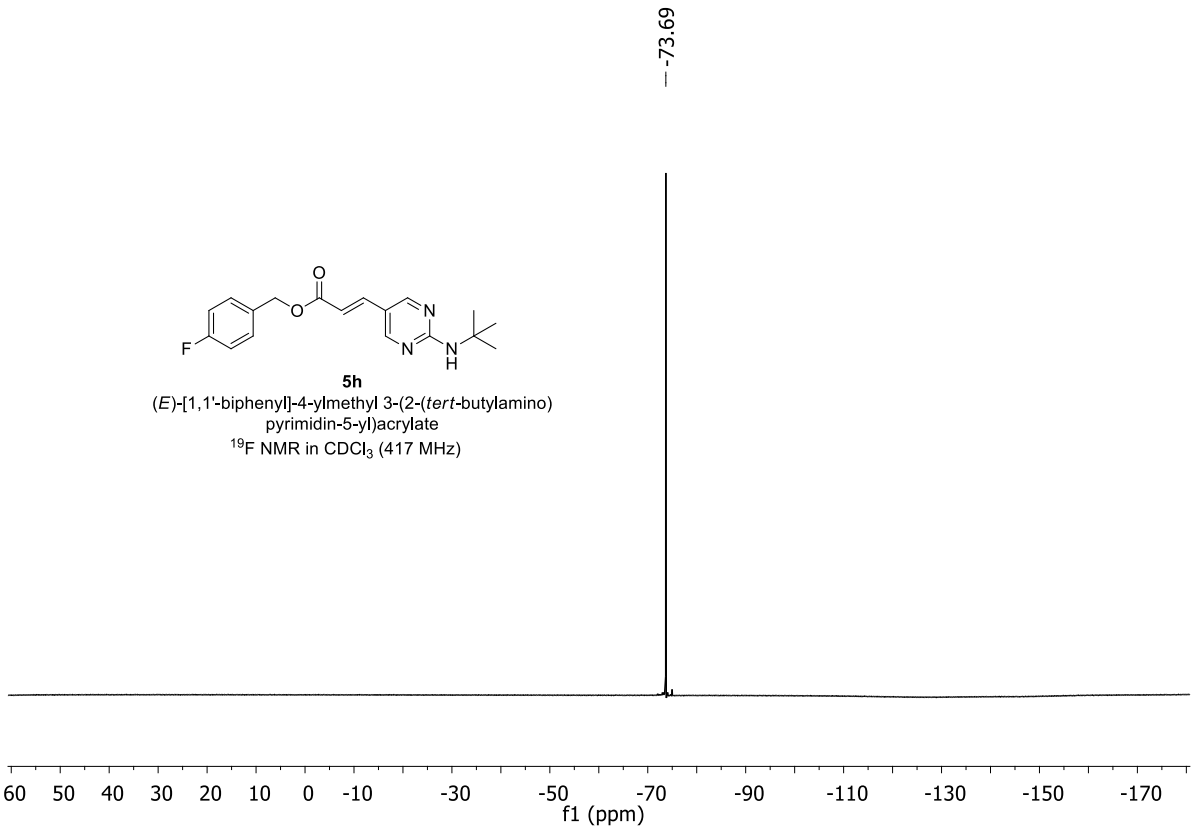
5g
(*E*)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(*tert*-butylamino) pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (126 MHz)



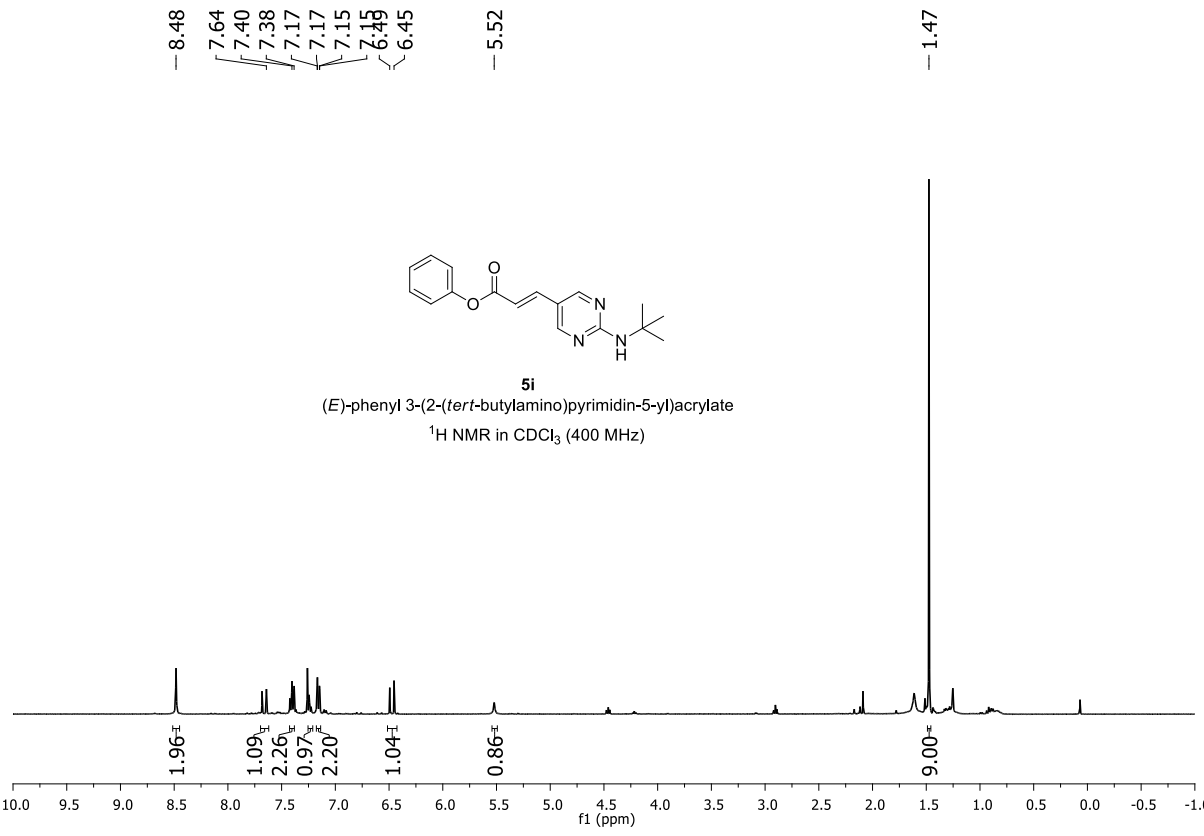
5h
(*E*)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(*tert*-butylamino) pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (400 MHz)



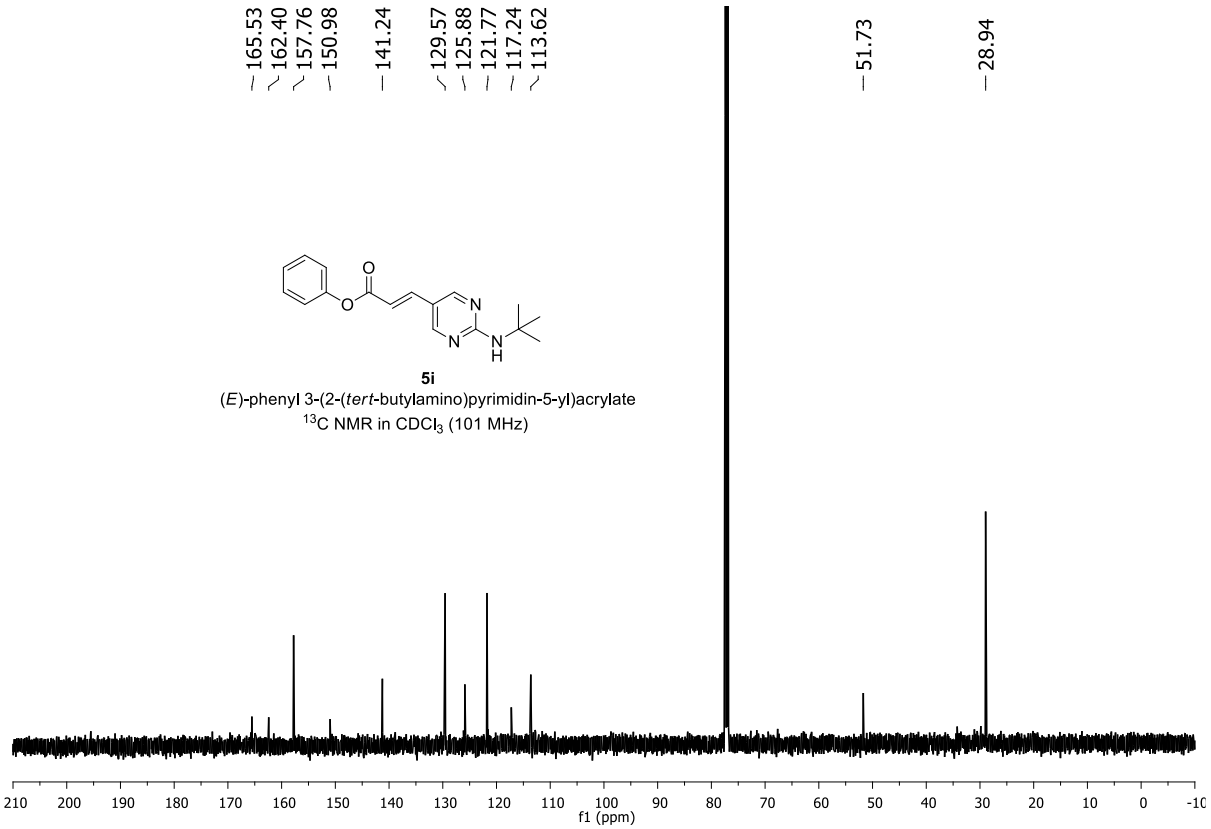
5h
(*E*)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(*tert*-butylamino) pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (101 MHz)



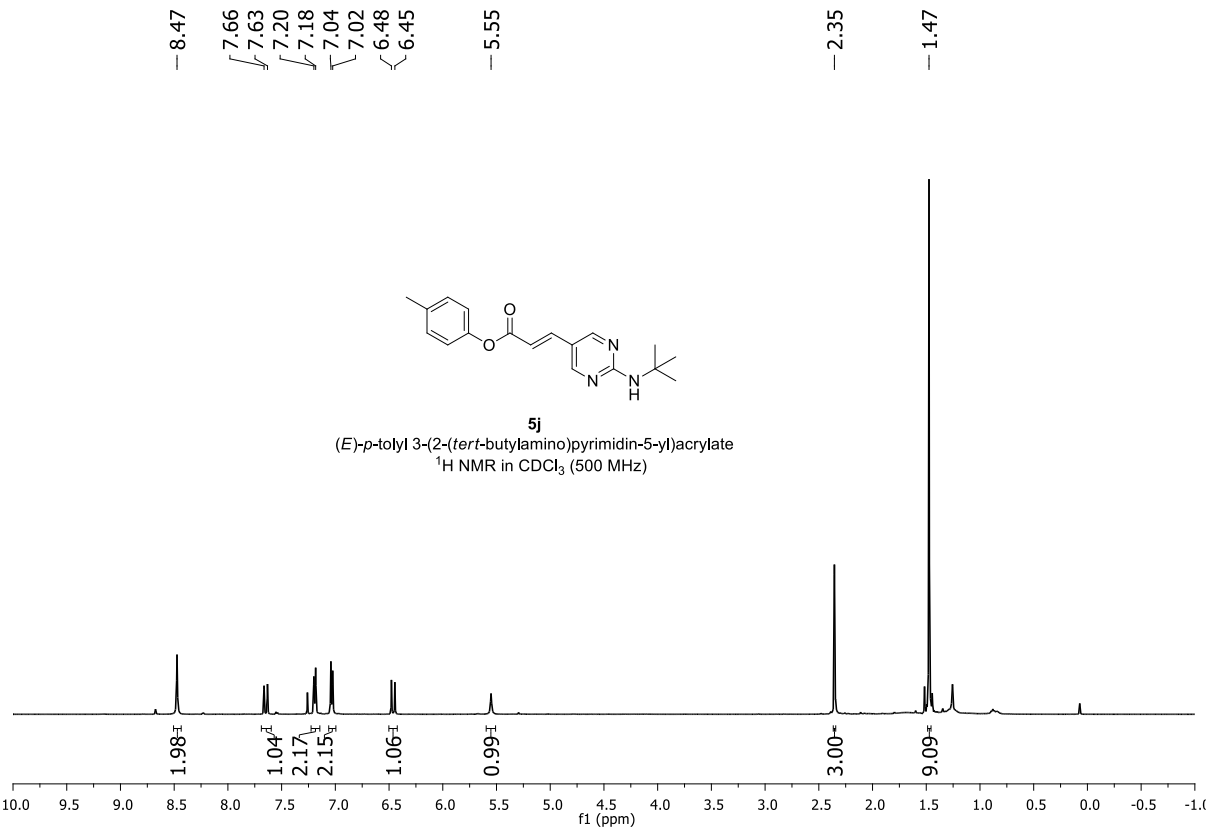
5h
(*E*)-[1,1'-biphenyl]-4-ylmethyl 3-(2-(*tert*-butylamino) pyrimidin-5-yl)acrylate
^{19}F NMR in $CDCl_3$ (417 MHz)



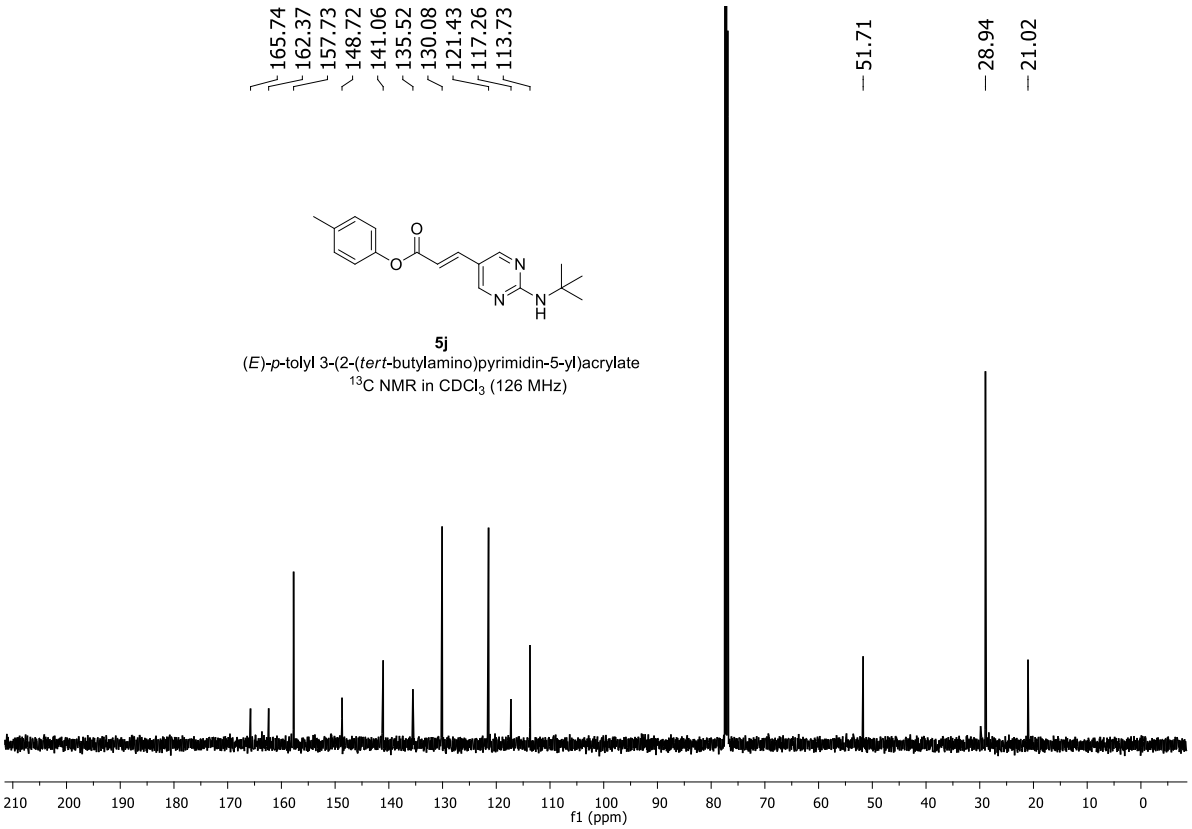
5i
(*E*)-phenyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (400 MHz)



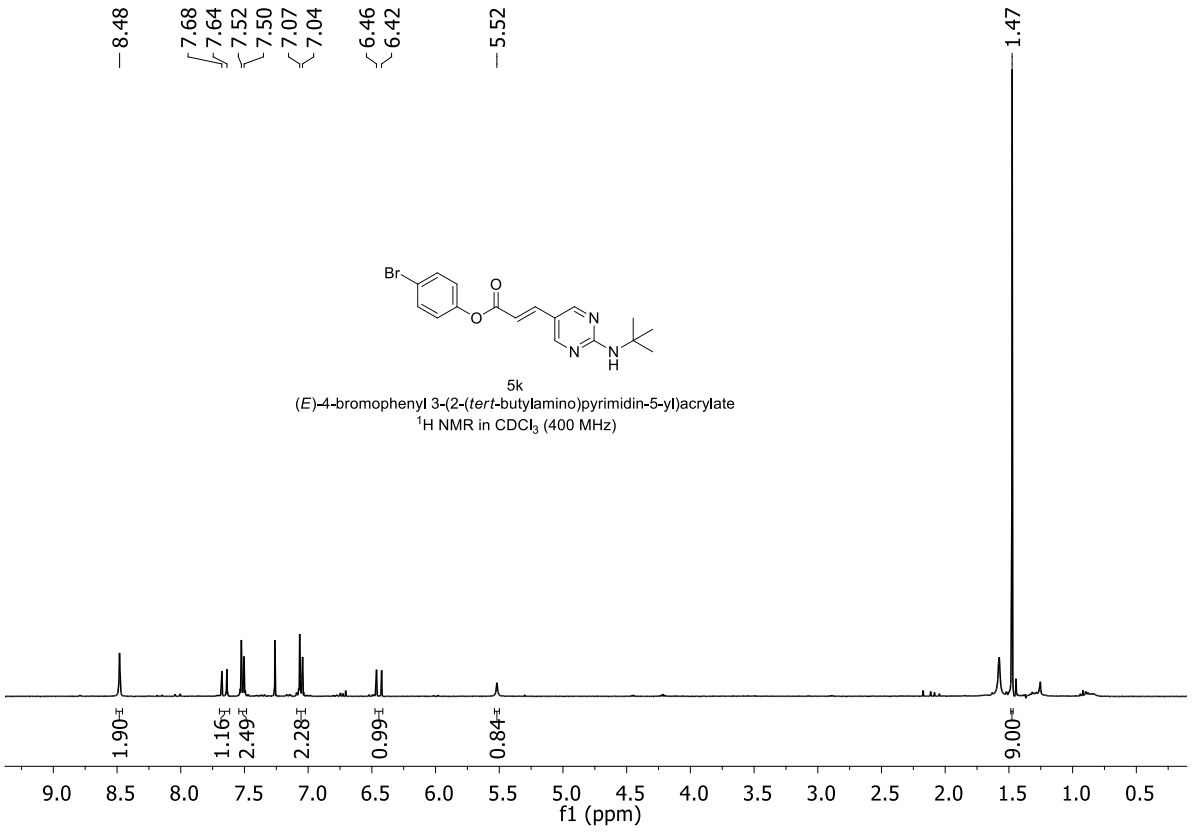
5i
(*E*)-phenyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (101 MHz)



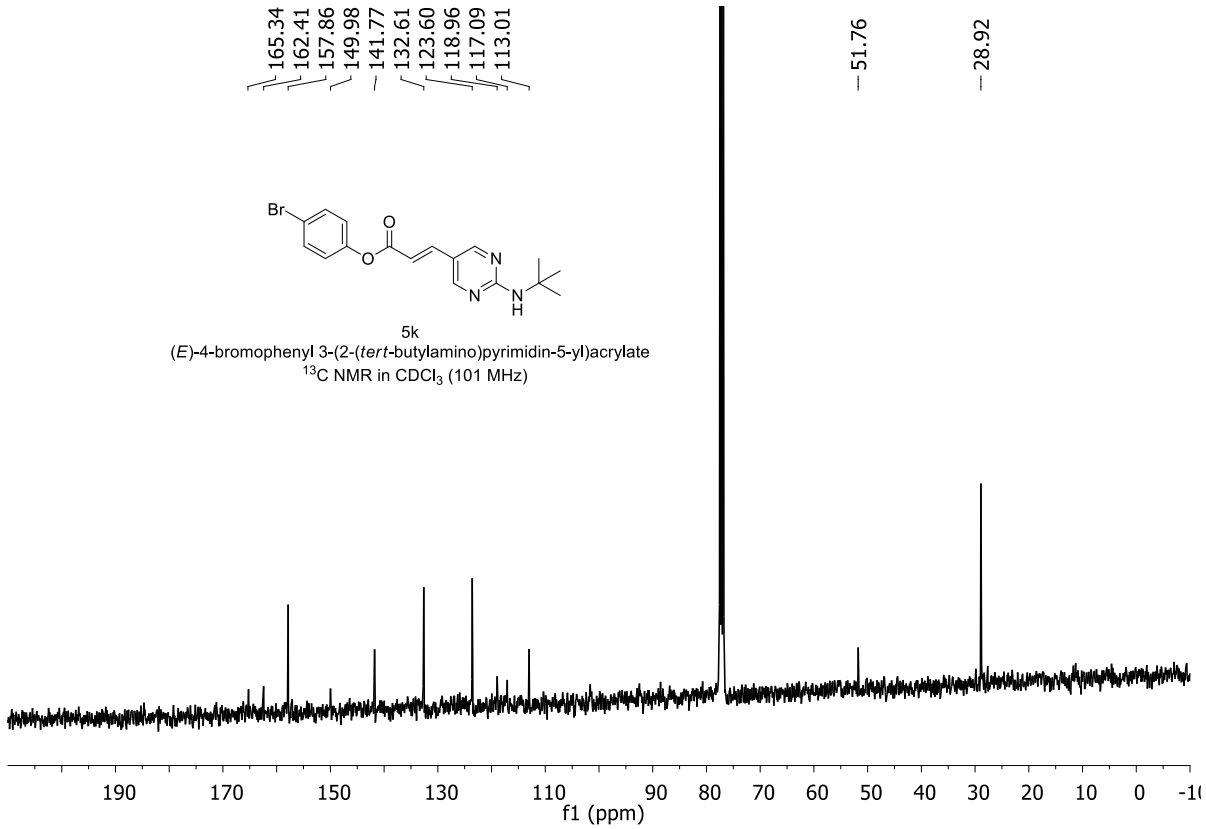
5j
(*E*)-*p*-tolyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (500 MHz)



5j
(*E*)-*p*-tolyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{13}C NMR in $CDCl_3$ (126 MHz)



5k
(*E*)-4-bromophenyl 3-(2-(*tert*-butylamino)pyrimidin-5-yl)acrylate
^{1}H NMR in $CDCl_3$ (400 MHz)



6. References

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