Mild and Highly Selective Palladium-Catalyzed Monoarylation of Ammonia Enabled by the Use of Bulky Biarylphosphine Ligands and Palladacycle Precatalysts

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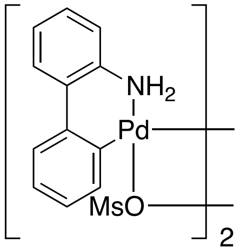
Supporting Information

General Analytical Information

Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz instruments at ambient temperature. All ^{1}H NMR spectra were measured in part per million (ppm) relative to the signals for tetramethylsilane (TMS) added into the deuterated chloroform ($CDCl_3$) (0 ppm), or the signals for residual dimethyl sulfoxide (DMSO) in deuterated DMSO (DMSO-d_6) (2.50 ppm), unless otherwise stated. Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, ovrlp = overlap, br = broad), coupling constants, and integration. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.16 ppm) or DMSO-d_6 (25.12 ppm) unless otherwise stated, and were obtained with complete ^{1}H decoupling. All GC analyses were performed on an Agilent 6890 gas chromatograph with a FID detector using a J&W DB-1 column (10 m, 0.1 mm I.D.). All GC-MS analyses were performed on an Agilent 6850 gas chromatograph with a 5975 inert mass selective detector. IR spectra were reported on a Nicolet iS5 FT-IR Spectrometer. Melting points (uncorrected) were obtained on a Mel-Temp II capillary melting point apparatus. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. ESI-MS spectra were recorded on a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS).

General Reagent Information

Unless otherwise noted, all chemicals used in the preparations of ligands and heteroaryl halides, and the (hetero)aryl halides used in the coupling with ammonia, were commercially available and were used as received without further purification. THF was purchased from J.T. Baker in CYCLE-TAINER® solvent-delivery kegs and vigorously purged with argon for 1 h. The THF solvent was further purified by passing it under argon pressure through two packed columns of neutral alumina. Anhydrous 1,4-dioxane (99.8%), and anhydrous ammonia solution (0.50 M in 1,4-dioxane, 100 mL) were purchased from Aldrich Chemical Co. in Seal-Seal® bottles and stored under argon. Sodium *tert*-butoxide was purchased from Aldrich Chemical Co. and the bulk was stored in a glove-box. Small quantities (~5 g) of sodium *tert*-butoxide was periodically transferred into a capped glass vial in the glove-box, taken out of the glove-box for use, and stored in the air in a desiccator cabinet (with anhydrous calcium sulfate). In order to ensure the reproducibility of the experimental results, it was recommended to consume the ammonia solution within 2 weeks once the bottle has first been used.[1] Ligand **L1** was purchased from Aldrich Chemical Co.. Pd_2dba_3 and ligand **L2** were purchased from Strem Chemicals, Inc.. Ligands **L3**,[2] **L4**,[3] and **L5**,[2] the palladacycle precatalyst precursor Pd μ-OMs dimer (**S1**),[4] the palladacycle precatalyst **3c**,[5] 1-benzyl-6-chloroindole (**S2**),[6] 4-bromo-1-trityl-1*H*-imidazole (**S3**),[7] and 4-bromo-1-trityl-1*H*-pyrazole **(S4)**[8] were prepared according to the literature procedures.



S1

General Considerations

All reactions for the palladium-catalyzed arylation of ammonia were set up on bench-top in the open air and carried out in re-sealable test tubes with Teflon septa under an argon atmosphere. Unless otherwise noted, the reaction test tubes were cooled to room temperature (if they were previously heated at elevated temperatures), prior to the transfers of compounds into the tubes or the purifications. Unless otherwise noted, the solutions of reagents / reactants were transferred via plastic syringe (fitted with metal needle) into the reaction test tubes under a positive argon pressure. Flash column chromatography was performed using silica gel (Silicycle, ultra pure grade) or alumina (Merck, Chromatographic Grade 80-200 Mesh). The solvent system as an eluent for column chromatography is presented as a ratio of solvent volumes. Yields reported in the publication are of isolated materials. The yields of arylamine products (anilines and heteroarylamines) represent an average of two independent runs unless otherwise noted. All arylamines were characterized by ^{1}H NMR and ^{13}C NMR spectroscopies and elemental analyses / high-resolution mass spectrometry. All unknown and most known arylamines were further characterized by IR spectroscopy and melting point determination (for solids). Unless otherwise noted, the formation of secondary diarylamine side-product was determined by GC/MS analysis, and the ratio of arylamine (1^o) to secondary diarylamine (2^o) (1^o : 2^o) was determined by ^{1}H NMR spectroscopy of the crude product based on 0.25 mmol of (hetero)aryl halide. In case the arylamine product and the diarylamine were inseparable by column chromatography, the 1^o : 2^o ratio was determined by ^{1}H NMR spectroscopy of the isolated mixture of arylamine and diarylamine. In case no diarylamine was detected by GC/MS analysis, the 1^o : 2^o ratio was assumed to be > 50 : 1.

Safety Precautions

All reactions with ammonia should be performed behind a blast shield, since high pressure can be built up inside the test tubes at elevated temperature and explosion of the tubes could occur.

Supplementary Experimental Results

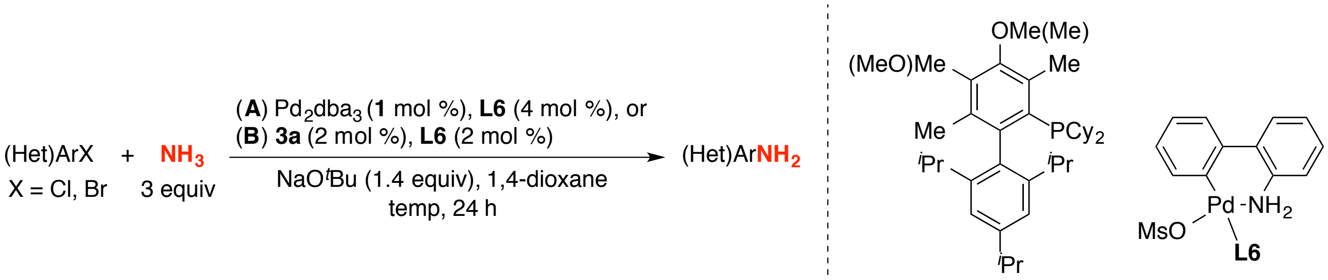
(A) Effect of palladium sources on the arylation of NH_3. The efficiency of two palladium sources, (**A**) Pd_2dba_3 and (**B**) precatalyst **3a**, were compared by using the identical Pd : **L6** ratio (Pd (2 mol %) : **L6** (2 mol %)) in the Pd-catalyzed coupling of ammonia with heteroaryl halides and heteroaryl-substituted aryl chloride (Table S1). Pd_2dba_3 and **3a** performed similarly to give similar yields of arylamines in the amination with 1-(4-chlorophenyl)imidazole, 2-chloro-6-(dimethylamino)pyrazine, 6-bromoquinoxaline and 3-bromo-5-methylpyridine (Table S1, entries 1-4). However, Pd_2dba_3 was found to be less effective than **3a** in the amination with 2-chloro-5-methylpyridine and 5-chlorobenzoxazole, since lower yields of arylamines were obtained with the use of Pd_2dba_3 (Table S1, entries 5 and 6). In addition, Pd_2dba_3 was less effective than **3a** in the amination with 6-chloroquinoline and 2-chloro-4,6-dimethoxypyrimidine, due to the incomplete conversion with the use of Pd_2dba_3 (Table S1, entries 7 and 8). While the use of premixed Pd_2dba_3/**L6**[9] led to complete conversion of 6-chloroquinoline, it did not lead to complete conversion of 2-chloro-4,6-dimethoxypyrimidine (Table S1, entries 7 and 8). Thus, **3a**/**L6** was selected as the catalyst system for the study of substrate scope of (hetero)aryl halides in the cross-coupling with ammonia.

(B) Effect of ligands on Pd-catalyzed coupling of NH_3 with sterically hindered (hetero)aryl halides and five-membered heteroaryl halides. The ligand effect on the coupling of NH_3 with sterically hinderd (hetero)aryl halides and five-membered heteroaryl halides was examined (Scheme S1). We found that the use of **L7** (with less bulky P-bound phenyl groups) allowed for the complete conversion of sterically hindered (hetero)aryl halides to the arylamines in excellent yields, whereas the use of **L4** (with the most bulkiest P-bound 1-adamantyl groups) allowed for the complete conversion of five-membered heteroaryl halide to the arylamines in high yield.

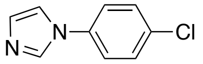
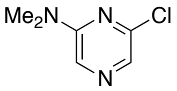
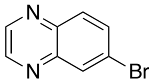
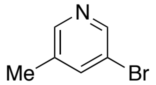
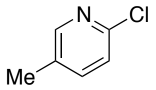
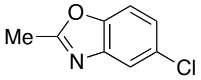
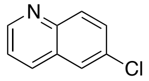
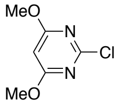
(C) Control experiments for the palladium-catalyzed arylation of NH_3. To ensure that the coupling of ammonia with electron-poor and activated (hetero)aryl halides is mediated by palladium rather than nucleophilic aromatic substitution, control experiments without the addition of precatalyst **3a** were carried out (Scheme S2). In the presence of **3a**, all (hetero)aryl halides were completely converted to the arylamine products. In contrast, when no **3a** was added, no arylamines or only traces of arylamines were detected (as shown in the parentheses in Scheme S2). The control experiments suggest that palladium-catalyzed arylation of ammonia does operate to yield the arylamines.

(D) Additional results for the palladium-catalyzed arylation of NH_3. The reaction protocols were also applicable for the coupling of ammonia with other (hetero)aryl halides (Scheme S3). The yields of the arylamine products were determined by ^1H NMR spectroscopy. The products were characterized by ^1H NMR spectroscopy and most of them were further characterized by GC/MS analysis. Of importance, some of the arylamine products were partially lost or decomposed during the column chromatography. However, some of the (hetero)aryl halides remained difficult coupling partners, including the aryl halides bearing acidic protons (-CO_2H, -OH, -C(O)NH_2) and the NH-unprotected heteroaryl halides (e.g. 5-chloroindole, 5-chlorobenzimidazole, 3-chloroindazole, 4-bromopyrazole, 4-bromo-2-methylimidazole).

Table S1. Effect of Pd Sources on the Arylation of NH_3[a]

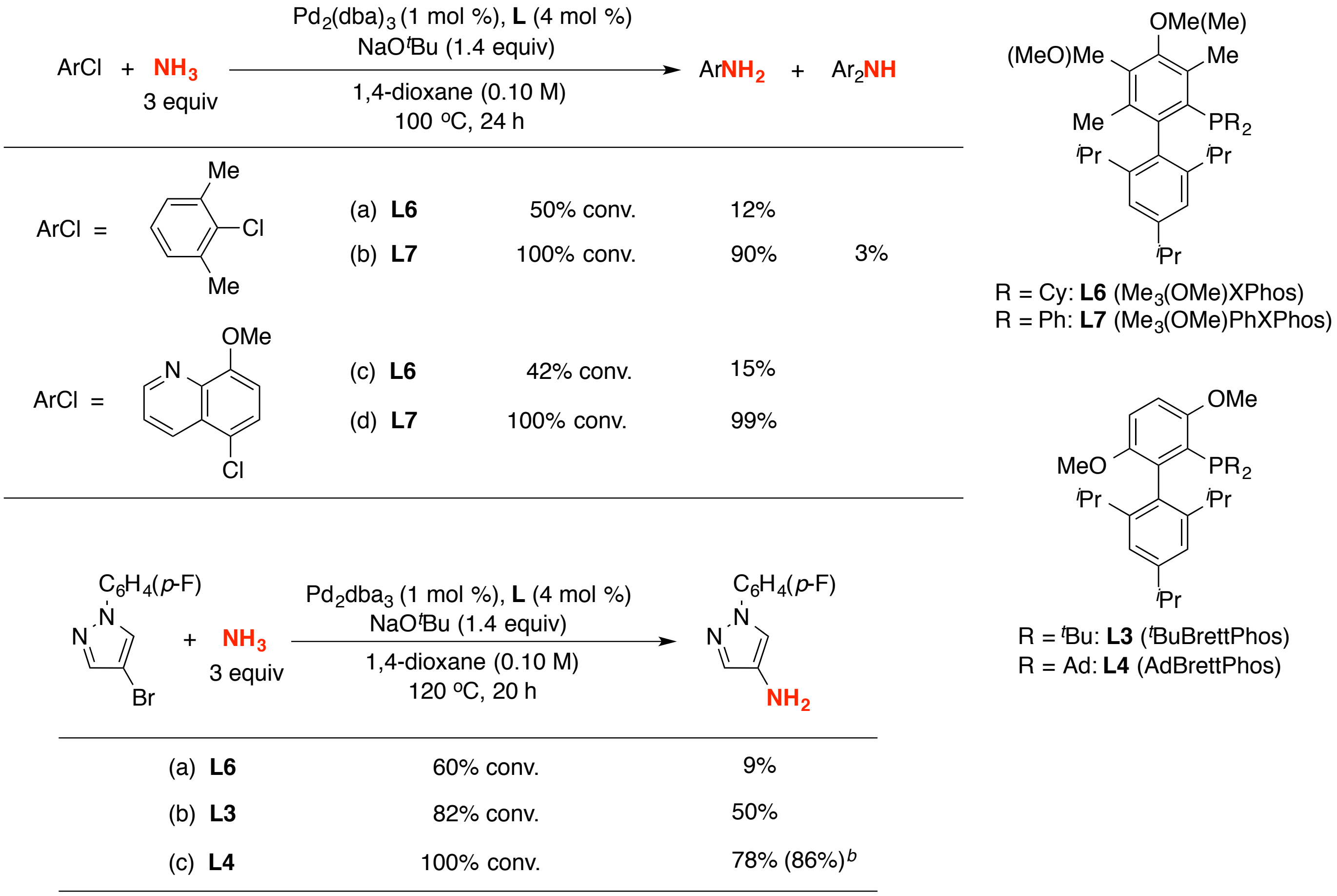


L6 (Me$_3$(OMe)XPhos) **3a**

Entry	(Het)ArX	Temp/°C	Pd source	Conversion/%[b]	Yield/%[b]
1		80	**(A)** Pd_2dba_3 **(B) 3a**	100 100	96 94
2		50	**(A)** Pd_2dba_3 **(B) 3a**	100 100	96 100
3		50	**(A)** Pd_2dba_3 **(B) 3a**	100 100	88 85
4		80	**(A)** Pd_2dba_3 **(B) 3a**	100 100	86 84
5		50	**(A)** Pd_2dba_3 **(B) 3a**	100 100	80 90
6		80	**(A)** Pd_2dba_3 **(B) 3a**	100 100	61 72
7		50	**(A)** Pd_2dba_3 **(B) 3a**	75 (100)[c] 100	75 (93)[c] 100
8		50	**(A)** Pd_2dba_3 **(B) 3a**	63 (55)[c] 100	36 (31)[c] 80[d]

[a] Reaction Conditions: HetArX (0.25 mmol), NH_3 (0.75 mmol, 3 equiv), NaO^{t}Bu (0.35 mmol, 1.4 equiv), Pd_2dba_3 (1 mol), **L6** (4 mol %), (or **3a** (2 mol %), **L6** (2 mol %)), 1,4-dioxane (2.5 mL, 0.10 M), 24 h. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] Pd_2dba_3 (1 mol %) and **L6** (4 mol %) were preheated in 1,4-dioxane (1.0 mL) at 100 °C for 3 min prior to the reaction. [d] Yield is of isolated product based on 1 mmol of HetArX (average of 2 runs).

Scheme S1. Effect of ligands on Pd-catalyzed coupling of NH_3 with sterically hindered (hetero)aryl halides and five-membered heteroaryl halides[a]

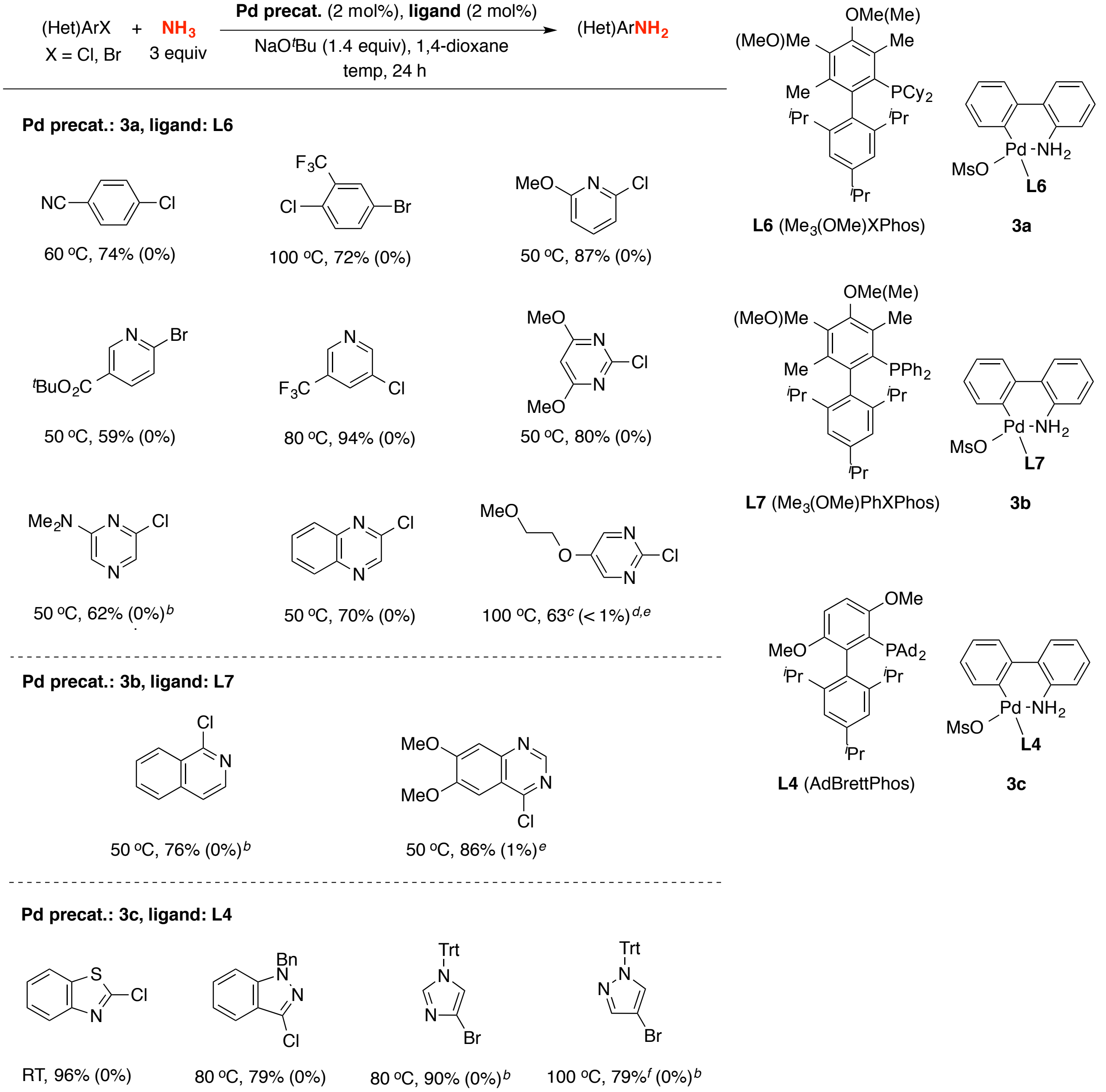


		$ArNH_2$	Ar_2NH
(a) **L6**	50% conv.	12%	
(b) **L7**	100% conv.	90%	3%
(c) **L6**	42% conv.	15%	
(d) **L7**	100% conv.	99%	

(a) **L6**	60% conv.	9%
(b) **L3**	82% conv.	50%
(c) **L4**	100% conv.	78% (86%)[b]

[a] Reaction Conditions: (Het)ArX (0.25 mmol), NH_3 (0.75 mmol, 3 equiv), NaO^{t}Bu (0.35 mmol, 1.4 equiv), Pd_2dba_3 (1 mol), ligand (4 mol %), 1,4-dioxane (2.5 mL, 0.10 M), 20-24 h; ^{1}H NMR yields were reported using 1,3,5-trimethoxybenzene as internal standard. [b] Isolated yield based on 1 mmol HetArX.

Scheme S2. Control experiments for the Pd-catalyzed arylation of NH_3[a]



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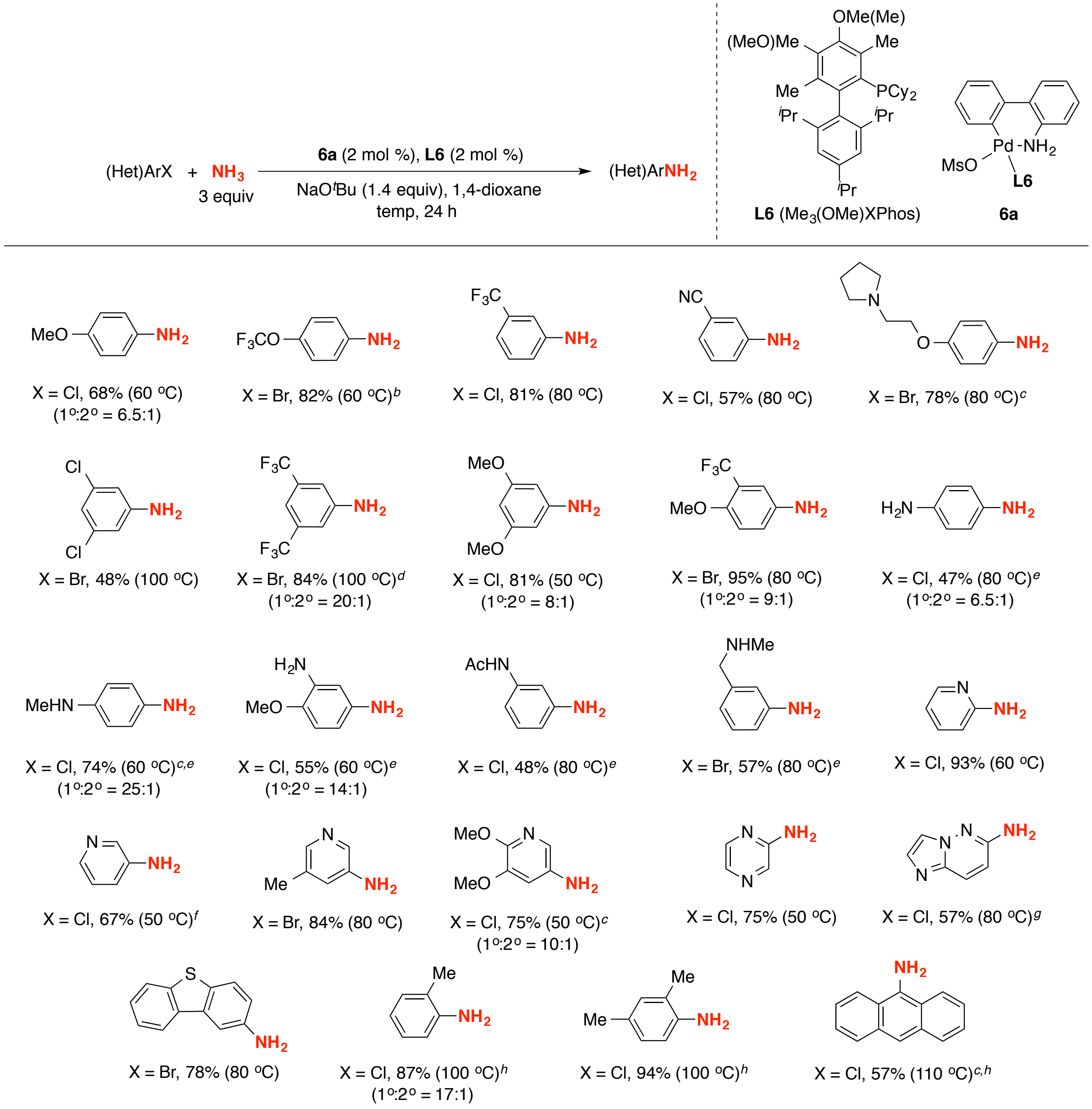
[a] **Reaction conditions with Pd and ligand:** HetArX (1 mmol), NH_3 (3 mmol), NaO^{t}Bu (1.4 mmol), precatalyst (2 mol %), ligand (2 mol %), 1,4-dioxane (10 mL, 0.10 M), 24 h; the yields are of isolated products. **Reaction conditions without Pd:** HetArX (0.25 mmol, 1 equiv), NH_3 (0.75 mmol, 3 equiv), NaO^{t}Bu (0.35 mmol, 1.4 equiv), ligand (2 mol %), 1,4-dioxane (2.5 mL, 0.10 M), 24 h; the yields in parentheses are of the arylamine products determined by GC/MS analysis. [b] The formation of product was judged by TLC analysis by comparing with authentic products. [c] HetArX (2 mmol, 1 equiv), NH_3 (6 mmol, 3 equiv), NaO^{t}Bu (2.8 mmol, 1.4 equiv) and 1,4-dioxane (13 mL, 0.154 M). [d] 1,4-dioxane (1.6 mL, 0.154 M). [e] The yield of product was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [f] 20 h.

Scheme S3. Additional results for the palladium-catalyzed arylation of NH_3[a]



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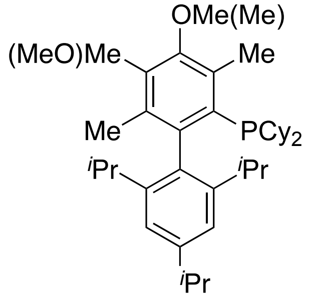
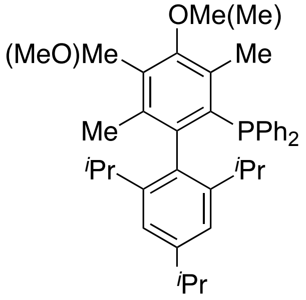
[a] Reaction conditions: HetArX (0.25 mmol, 1 equiv), NH_3 (0.75 mmol, 3 equiv), NaO*t*Bu (0.35 mmol, 1.4 equiv), **3a** (2 mol %), **L6** (2 mol %), 1,4-dioxane (2.5 mL, 0.10 M), 24 h; the yield and the ratio of primary to secondary amine (1°:2°) were determined by ^1H NMR spectroscopy. [b] The product was isolated in low yield upon column chromatography likely due to its volatility. [c] The product decomposed to an unknown product mixture or was partially lost upon column chromatography. [d] 16 h. [e] NaO*t*Bu (0.55 mmol, 2.2 equiv). [f] GC yield using *n*-dodecane as internal standard. [g] HetArCl in the form of HetArCl·HCl; NaO*t*Bu (0.60 mmol, 2.4 equiv). [h] **3b** (2 mol %) / **L7** (2 mol %).

Preparations of Biaryl Phosphine Ligands (L6-L9):



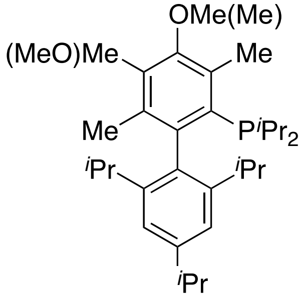
Me_3(OMe)XPhos

Dicyclohexyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Dicyclohexyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (Me_3(OMe)XPhos (L6)). An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with magnesium turnings (486 mg, 20.0 mmol, 4.0 equiv). Tube **A** was then evacuated and backfilled with argon (this sequence was repeated a total of three times). 2-Bromo-1,3,5-triisopropylbenzene (1.26 mL, 5.0 mmol, 1.0 equiv), 1,2-dibromobenzene (40 μL), and THF (8.0 mL) were added into tube **A** via syringe. Tube **A** was then stirred at 80 °C in an oil bath for 1.5 h to form a Grignard reagent. Simultaneously, an oven-dried 20 mL re-sealable screw-cap test tube (**B**) was charged with 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene (1.85 g, 6.0 mmol, 1.2 equiv). Tube **B** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and THF (4.0 mL) was added into the tube via syringe. The solution of 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene from tube **B** was then transferred into the Grignard reagent of 2-bromo-1,3,5-triisopropylbenzene in tube **A** followed by the addition of 1,2-dibromobenzene (40 μL) via syringe. The reaction mixture in tube **A** was then stirred at 80 °C in an oil bath for 1 h; at this time, 1,2-dibromobenzene (20 μL) was added via a syringe, and the reaction mixture was stirred at 80 °C for 1 h (this sequence was repeated a total of two times). Finally, 1,2-dibromobenzene (40 μL) was added via syringe, and the resulting reaction mixture in tube **A** was stirred at 80 °C for 2 h. An oven-dried 25 mL re-sealable screw-cap test tube (**C**) equipped with a Teflon-coated magnetic stir bar was charged with copper(I) chloride (495 mg, 5.0 mmol, 1.0 equiv), and the tube was evacuated and backfilled with argon (this sequence was repeated a total of three times). The hot reaction mixture from tube **A** was quickly and carefully cannulated (Note: Caution!) into tube **C**.[10] Chlorodicyclohexylphosphine (1.3 mL, 6.0 mmol, 1.2 equiv) was added into tube **C** via syringe, and the tube was heated at 80 °C in an oil bath for 24 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (~50 mL), washed with aqueous ammonia solution (27-30%) until the aqueous fraction was colorless, and then was washed with saturated NaCl solution. The organic fraction was dried over Na_2SO_4, and concentrated *in vacuo* with the aid of a rotary evaporator to give a yellow crude oil. The crude oil was diluted with EtOAc (~5 mL) and then MeOH (~50 mL) was added. The mixture was cooled to 0 °C overnight to obtain a white precipitate. The solid so formed was isolated by filtration, washed with cold MeOH, and dried *in vacuo*. A white powdery solid **L6** (1.65 g, 3.01 mmol, 60%) was obtained as an 1.3 : 1.0 mixture of two isomers as determined by the methoxy proton signals by ^{1}H NMR spectroscopy (methoxy proton of major isomer: 3.73 ppm; minor isomer: 3.66 ppm). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.96 (s, 2 H), 3.73 (s, 1.7 H), 3.66 (s, 1.3 H), 2.92 (sep, *J* = 6.8 H, 1 H), 2.43-2.34 (ovrlp, 5 H), 2.25 (s, 1.3 H), 2.19 (s, 1.7 H), 2.04-1.99 (m, 2 H), 1.80-1.78 (m, 2 H), 1.66-1.63 (ovrlp, 9 H), 1.41-1.38 (m, 2 H), 1.29 (d, *J* = 7.2 Hz, 6 H), 1.25-1.09 (ovrlp, 14 H), 1.01-0.89 (ovrlp, 8 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 157.9, 155.4, 149.1, 148.7, 147.1, 145.68, 145.66, 145.5, 145.32, 145.30, 145.1, 141.7, 141.6, 137.9, 137.8, 137.6, 137.5, 135.9, 135.8, 133.8, 133.7, 133.2, 132.9, 131.0, 130.1, 129.9, 128.6, 128.5, 128.0, 59.8, 59.5, 39.9, 39.8, 39.3, 39.1, 34.5, 34.4, 34.2, 34.1, 34.0, 30.4, 30.32, 30.27, 30.24, 30.18, 28.2, 28.1, 28.0, 27.8, 27.6, 26.5, 25.09, 25.06, 25.0, 24.8, 24.2, 20.2, 19.9, 19.8, 15.90, 15.87, 15.8, 13.5, 13.3 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 2.3, 0.8. **IR** (neat cm^{-1}) 2930, 2847, 1458, 1379, 1219, 1086, 1002, 874. **Anal.** Calcd. for $C_{37}H_{57}OP$: C, 80.97; H, 10.47; Found: C, 80.97; H, 10.38.



Me$_3$(OMe)PhXPhos

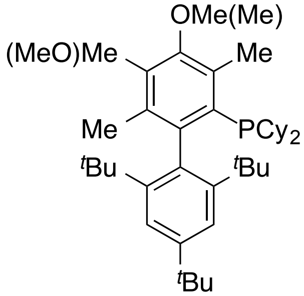
Diphenyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Diphenyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (Me$_3$(OMe)PhXPhos (L7)). The procedure to prepare **L6** was employed except that magnesium turnings (292 mg, 12.0 mmol, 4.0 equiv) and 2-bromo-1,3,5-triisopropylbenzene (0.76 mL, 3.0 mmol, 1.0 equiv) in THF (5 mL), 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene (1.11 g, 3.6 mmol, 1.2 equiv) in THF (2 mL), copper(I) chloride (327 mg, 3.3 mmol, 1.1 equiv), and chlorodiphenylphosphine (0.71 mL, 3.3 mmol, 1.1 equiv), were used. A white powdery solid **L7** (802 mg, 1.49 mmol, 50%) was obtained as a 1.3 : 1.0 mixture of two isomers as determined by the methoxy proton signals by ^{1}H NMR spectroscopy (methoxy proton of major isomer: 3.77 ppm; minor isomer: 3.70 ppm). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.30-7.15 (ovrlp, 10 H), 6.93 (s, 2 H), 3.77 (s, 1.7 H), 3.70 (s, 1.3 H), 2.89 (sep, *J* = 6.8 Hz, 1 H), 2.49-2.42 (ovrlp, 2 H), 2.31 (s, 1.3 H), 2.24 (s, 1.7 H), 1.87 (s, 1.7 H), 1.84 (s, 1.3 H), 1.78 (s, 1.3 H), 1.77 (s, 1.7 H), 1.25 (d, *J* = 6.8 Hz, 6 H), 1.00-0.96 (ovrlp, 6 H), 0.70-0.68 (ovrlp, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 159.1, 156.8, 149.4, 149.0, 147.5, 146.11, 146.09, 145.77, 145.75, 145.6, 145.2, 142.64, 142.60, 138.4, 138.2, 138.1, 137.9, 137.2, 137.1, 136.8, 136.7, 135.7, 135.6, 135.0, 134.9, 132.8, 132.1, 131.9, 131.7, 131.6, 131.3, 131.13, 131.09, 131.0, 130.1, 129.2, 129.1, 128.5, 128.4, 128.2, 127.0, 126.9, 120.9, 120.8, 60.0, 59.91, 59.87, 59.8, 34.0, 30.7, 30.6, 25.02, 24.96, 24.4, 24.2, 23.9, 23.7, 23.6, 22.1, 19.19, 19.15, 17.5, 15.3, 13.6, 13.4 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: -11.8, -12.6. **IR** (neat cm^{-1}) 2958, 2865, 1478, 1432, 1381, 1230, 1088, 876, 747, 739. **HRMS** (ESI) Calcd for $C_{37}H_{45}OP$ [M+H]: 537.3281; Found: 537.3283.



Me$_3$(OMe)^{i}PrXPhos

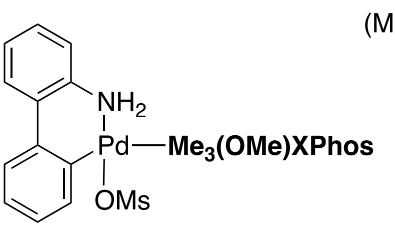
Diisopropyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Diisopropyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (Me$_3$(OMe)^{i}PrXPhos (L8)). An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with magnesium turnings (292 mg, 12.0 mmol, 4.0 equiv). Tube **A** was then evacuated and backfilled with argon (this sequence was repeated a total of three times). 2-Bromo-1,3,5-triisopropylbenzene (0.76 mL, 3.0 mmol, 1.0 equiv), 1,2-dibromobenzene (20 μL), and THF (5.0 mL) were added into the tube via syringe. The tube was then stirred at 80 °C in an oil bath for 1.5 h to form a Grignard reagent. Simultaneously, an oven-dried 20 mL re-sealable screw-cap test tube (**B**) was charged with 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene (1.11 g, 3.6 mmol, 1.2 equiv). Tube **B** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and THF (2.0 mL) was added into the tube via syringe. The solution of 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene from tube **B** was then transferred into the Grignard reagent of 2-bromo-1,3,5-triisopropylbenzene in tube **A** followed by the addition of 1,2-dibromobenzene (20 μL) via syringe. The reaction mixture in tube **A** was then stirred at 80 °C in an oil bath for 1 h; at this time, 1,2-dibromobenzene (10 μL) was added via syringe, and the reaction mixture was further stirred at 80 °C for 1 h (this sequence was repeated a total of two times). Finally, 1,2-dibromobenzene (20 μL) was added via syringe, and the reaction mixture in tube **A** was further stirred at 80 °C for 2 h. After cooling to room temperature, copper(I) chloride (297 mg, 3.0 mmol, 1.0 equiv) was quickly transferred into tube **A** under a positive argon pressure. Chlorodiisopropylphosphine (0.71 mL, 3.3 mmol, 1.1 equiv) was then added into tube **A** via syringe, and the reaction mixture was stirred at 80 °C in an oil bath for 18 h. The reaction mixture was diluted with EtOAc (~50 mL), washed with aqueous ammonia solution (27-30%) until the aqueous fraction was colorless, and then washed with saturated NaCl solution. The organic fraction was dried over Na$_2$SO$_4$, and concentrated *in vacuo* with the aid of a rotary evaporator to give a yellow crude oil. The crude oil was diluted with EtOAc (~3 mL) and then MeOH (~30 mL) was added. The mixture was cooled to 0 °C overnight to obtain a white precipitate. The solid so formed was isolated by filtration, washed with cold MeOH, and dried *in vacuo*. A white powdery solid **L8** (260 mg, 0.56 mmol, 18%) was obtained as a 1.1 : 1.0 mixture of two isomers as determined by the methoxy proton signals by ^{1}H NMR spectroscopy (methoxy proton of major isomer: 3.73 ppm; minor isomer: 3.66 ppm). **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 6.97 (s, 0.9 H), 6.96 (s, 1.1 H), 3.73 (s, 1.6 H), 3.66 (s, 1.4 H), 2.93 (sep, *J* = 6.8 Hz, 1 H), 2.45-2.36 (ovrlp, 5 H), 2.30-2.20 (ovrlp, 5 H), 1.67 (s, 1.4 H), 1.64 (s, 1.6 H), 1.30 (d, *J* = 6.8 Hz, 6 H), 1.17 (d, *J* = 6.8 Hz, 6 H), 1.15-1.08 (m, 6 H), 0.94-0.85 (ovrlp, 12 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 158.02, 158.00, 155.7, 149.2, 148.7, 147.2, 145.68, 145.66, 145.4, 145.32, 145.30, 145.03, 141.21, 141.16, 137.79, 137.69, 137.5, 137.4, 135.85, 135.76, 135.0, 134.7, 133.30, 133.26, 132.0, 131.7, 131.0, 128.5, 128.4, 128.3, 120.8, 120.7, 59.9, 59.6, 34.1, 30.39, 30.36, 29.0, 28.9, 28.4, 28.2, 25.1, 25.0, 24.78, 24.77, 24.64, 24.62, 24.3, 23.7, 23.5, 23.4, 23.2, 21.2, 21.1, 21.0, 20.2, 19.79, 19.75, 15.82, 15.79, 15.76, 13.5, 13.3 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, CDCl$_3$) δ: 19.7, 18.3. **IR**

(neat cm^{-1}) 2957, 2924, 2865, 1457, 1380, 1218, 1088, 1000, 876, 630. **Anal.** Calcd. for $C_{31}H_{49}OP$: C, 79.44; H, 10.54; Found: C, 79.41; H, 10.70.

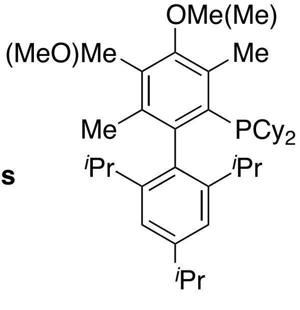


Dicyclohexyl(2',4',6'-tri-*tert*-butyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Dicyclohexyl(2',4',6'-tri-*tert*-butyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (L9). The procedure to prepare **L6** was employed except that magnesium turnings (292 mg, 12.0 mmol, 4.0 equiv) and 2-bromo-1,3,5-tri-*tert*-butylbenzene (976 mg, 3.0 mmol, 1.0 equiv) in THF (5 mL), 1,2-dibromo-4-methoxy-3,5,6-trimethylbenzene (1.11 g, 3.6 mmol, 1.2 equiv) in THF (3 mL), copper(I) chloride (297 mg, 3.0 mmol, 1.0 equiv), and chlorodicyclohexylphosphine (0.70 mL, 3.15 mmol, 1.05 equiv), were used. A white powdery solid **L9** (1.14 g, 1.93 mmol, 64%) was obtained as a 1.0 : 1.0 mixture of two isomers as determined by the methoxy proton signals by ^{1}H NMR spectroscopy (methoxy proton: 3.67 and 3.65 ppm).**^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.37 (s, 2 H), 3.67 (s, 1.5 H), 3.65 (s, 1.5 H), 2.36 (s, 1.5 H), 2.33 (s, 1.5 H), 2.23 (s, 1.5 H), 2.18 (s, 1.5 H), 2.07-1.97 (ovrlp, 5 H), 1.90-1.85 (m, 2 H), 1.71-1.69 (m, 2 H), 1.63-1.57 (m, 4 H), 1.33 (s, 9 H), 1.28-1.09 (m, 10 H), 1.06-0.90 (ovrlp, 20 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.7, 156.3, 150.9, 150.5, 147.64, 147.58, 147.3, 146.52, 146.51, 146.27, 146.26, 139.6, 139.5, 137.9, 137.6, 136.2, 136.1, 135.2, 134.9, 134.5, 134.4. 134.1, 134.0, 131.82, 131.78, 129.5, 129.4, 128.3, 128.1, 124.1, 123.9, 60.3, 59.3, 38.83, 38.78, 34.74, 34.73, 34.4, 34.22, 34.17, 34.15, 34.12, 34.1, 34.0, 33.8, 32.99, 32.95, 32.8, 32.7, 31.7, 31.6, 31.5, 31.4, 27.9, 27.79, 27.76, 27.66, 27.51, 27.47, 27.43, 27.40, 26.58, 26.57, 20.5, 20.4, 20.3, 16.63, 16.60, 16.2, 13.3, 13.2 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 6.6, 4.5. **IR** (neat cm^{-1}) 2923, 2847, 1446, 1374, 1214, 1083, 1001, 885, 851, 630. **Anal.** Calcd. for $C_{40}H_{63}OP$: C, 81.30; H, 10.75; Found: C, 81.45; H, 10.91.

Preparations of Palladcycle Preatalyst (3a, 3b):

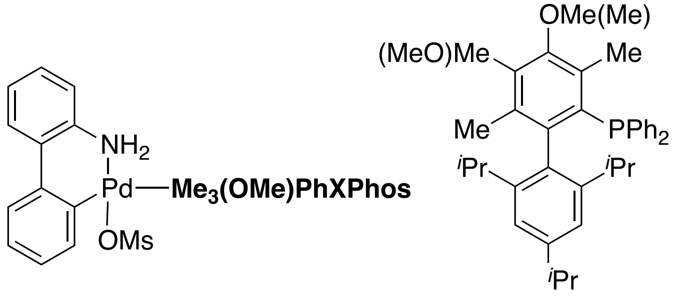


precatalyst 3a



Me3(OMe)XPhos

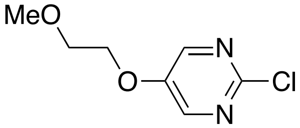
Palladacycle Precatalyst 3a. An oven-dried 100 mL round-bottomed flask equipped with a Teflon-coated magnetic stir bar and capped with a rubber septum was charged with Pd μ-OMs dimer (**S1**) (1.60 g, 2.16 mmol, 0.5 equiv) and **L6** (2.38 g, 4.33 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon (this sequence was repeated a total of three times), and THF (20 mL) was added into the flask via syringe. The reaction mixture was then stirred at room temperature for 1.5 h. The reaction mixture was concentrated *in vacuo* to give crude solid residue with the aid of a rotary evaporator. The residue was dissolved with ethyl acetate (~5 mL) followed by the addition of pentane (~20 mL). The solid that formed was triturated with the aid of an ultrasonic water-bath at room temperature. The resulting solid was filtered, washed with pentane, and dried *in vacuo* to afford a brownish-yellow solid **3a** (3.77 g, 4.10 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.62-7.61 (m, 1 H), 7.38-7.36 (m, 1 H), 7.33-7.29 (ovrlp, 2 H), 7.16-7.07 (ovrlp, 5 H), 6.84-6.82 (m, 1 H), 6.77-6.71 (m, 1 H), 3.75 (s, 1.8 H), 3.64 (s, 1.2 H), 3.49 (sep, *J* = 6.8 Hz, 1 H), 3.02-2.90 (m, 1 H), 2.73 (sep, *J* = 6.8 Hz, 1 H), 2.45 (s, 1.8 H), 2.41 (s, 1.2 H), 2.35-2.17 (ovrlp, 7 H), 2.00-1.81 (ovrlp, 8 H), 1.72-1.49 (ovrlp, 10 H), 1.42-1.20 (ovrlp, 8 H), 1.15-1.07 (ovrlp, 6 H), 1.00-0.68 (ovrlp, 11 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 160.1, 157.5, 157.4, 155.7, 155.5, 154.6, 154.3, 152.7, 152.6, 144.4, 144.2, 142.6, 142.3, 140.7, 140.5, 140.43, 140.39, 140.1, 139.9, 137.6, 137.5, 136.7, 135.1, 133.8, 133.7, 132.7, 132.3, 131.9, 131.7, 131.6, 130.5, 130.4, 129.3, 129.0, 128.0, 127.8, 126.7, 126.33, 126.29, 125.6, 125.2, 123.1, 122.25, 122.21, 60.2. 59.6, 39.0, 37.2, 37.0, 36.9, 36.6, 35.8, 35.6, 34.09, 34.05, 33.7, 33.34, 33.27, 33.1, 30.8, 29.6, 29.4, 29.1, 28.0, 27.9, 27.5, 27.0, 26.9, 26.2, 25.8, 25.7, 25.6, 25.4, 24.7, 24.6, 24.4, 22.3, 21.7, 18.5, 17.2, 14.2, 14.0 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 41.5, 41.2. **IR** (neat cm^{-1}) 2955, 2924, 2849, 1460, 1384, 1238, 1145, 1085, 1031, 1002, 730. **HRMS** (ESI) Calcd for $C_{50}H_{70}NO_4PPdS$ [M-OMs]: 822.4010; Found: 822.4001.



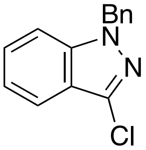
precatalyst 3b **Me$_3$(OMe)PhXPhos**

Palladacycle Precatalyst 3b. The procedure to prepare **3a** was employed, except that an oven-dried 25 mL re-sealable screw-cap test tube, Pd *μ*-OMs dimer (**S1**) (380 mg, 0.51 mmol, 0.5 equiv), **L7** (552 mg, 1.03 mmol, 1.0 equiv), and THF (10 mL) were used. The reaction mixture was then stirred at room temperature for 4 h. A brownish-yellow solid of **3b** (825 mg, 0.91 mmol, 88%) was obtained. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.61 (s, 1 H), 7.58-7.53 (m, 1 H), 7.47-7.44 (m, 2 H), 7.36-7.26 (ovrlp, 4 H), 7.23-7.14 (ovrlp, 4 H), 7.05-6.95 (ovrlp, 3 H), 6.90-6.83 (ovrlp, 2 H), 6.00-5.93 (m, 1 H), 3.73 (1.3 H), 3.69 (1.7 H), 3.46 (sep, *J* = 6.8 Hz, 1 H), 2.89-2.82 (m, 1 H), 2.35 (s, 3 H), 2.67 (s, 1.7 H), 2.22 (s, 1.3 H), 2.01 (sep, *J* = 6.8 Hz, 1H), 1.94-1.90 (ovrlp, 3 H), 1.70-1.69 (ovrlp, 3 H), 1.53-1.49 (ovrlp, 6 H), 1.36-1.25 (ovrlp, 3 H), 1.23-1.18 (ovrlp, 4 H), 0.77-0.73 (ovrlp, 3 H), (-0.20)-(-0.23) (ovrlp, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 161.29, 161.27, 157.9, 157.8, 154.5, 154.3, 152.5, 152.2, 150.9, 145.1, 144.91, 144.88, 144.8, 144.7, 144.6, 141.6, 141.2, 141.0, 139.4, 139.3, 138.7, 138.6, 137.1, 137.0, 136.89, 136.88, 136.86, 136.85, 136.83, 136.81, 135.84, 135.82, 135.8, 135.7, 134.2, 133.2, 133.09, 133.06, 133.0, 132.74, 132.67, 133.2, 133.09, 133.06, 133.0, 132.74, 132.67, 131.31, 131.29, 131.2, 131.1, 131.04, 130.99, 130.96, 130.89, 130.86, 130.80, 130.3, 130.1, 130.0, 129.6, 129.51, 129.48, 129.45, 129.4, 129.3, 129.1, 128.82, 128.79, 128.71, 128.69, 128.4, 127.9, 127.6, 126.8, 126.6, 126.50, 126.48, 125.7, 125.42, 125.35, 125.2, 125.1, 124.8, 123.23, 123.18, 122.7, 122.6, 121.82, 121.77, 120.2, 60.2, 59.9, 39.0, 33.9, 33.8, 33.0, 32.9, 31.53, 21.46, 26.4, 26.3, 24.60, 24.56, 24.48, 24.46, 24.43, 23.8, 22.6, 22.5, 21.12, 21.08, 17.8, 17.7, 16.6, 16.5, 13.8, 13.5, 13.2 (Observed complexity due to C-P splitting). **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 29.5, 29.4. **IR** (neat cm^{-1}) 2960, 1564, 1439, 1387, 1211, 1195, 1150, 1094, 1035, 1001, 884, 753, 701. **HRMS** (ESI) Calcd for $C_{50}H_{58}NO_4PPdS$ [M-OMs]: 810.3071; Found: 810.3054.

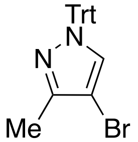
Preparation of Heteroaryl Halides



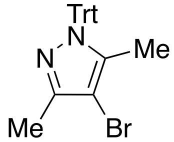
2-Chloro-5-(2-methoxyethoxy)pyrimidine (S5).[11] An oven-dried 25 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with 2-chloro-5-hydroxypyrimidine (2.61 g, 20 mmol, 1.0 equiv), 1-bromo-2-methoxyethane (2.3 mL, 24 mmol, 1.2 equiv), potassium carbonate (3.59 g, 26 mmol, 1.3 equiv), and DMF (10 mL). The sealed tube was then stirred at 100 °C in an oil bath for 4 h. After cooling to room temperature, the reaction mixture was washed with water (200 mL) and EtOAc (50 mL). The aqueous layer was further extracted with EtOAc (2 x 50 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using EtOAc / hexanes (1:1) as an eluent to give a white solid. The white solid was dissolved in EtOAc (~5 mL) and was then triturated with hexanes (~50 mL) to give a white solid. The white solid was filtered and dried *in vacuo* to afford 2-chloro-5-(2-methoxyethoxy)pyrimidine (**S6**) (2.36 g, 12.5 mmol, 63%). **m.p.:** 58-59 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.35 (s, 2 H), 4.24 (t, J = 4.4 Hz, 2 H), 3.78 (t, J = 4.4 Hz, 2 H), 3.45 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.4, 152.2, 146.4, 70.6, 68.8, 59.3. **IR** (neat cm^{-1}) 2939, 1574, 1550, 1407, 1379, 1278, 1197, 1118, 1034, 964, 915, 858, 757, 685, 630. **Anal.** Calcd. for $C_7H_9ClN_2O_2$: C, 44.58; H, 4.81; Found: C, 44.57; H, 4.82.



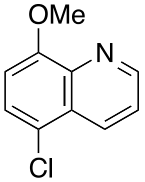
1-Benzyl-3-chloro-1*H*-indazole (S6). A 100 mL conical flask (**A**) equipped with a Teflon-coated magnetic stir bar and capped with a rubber septum was charged with 3-chloro-1*H*-indazole (2.30 g, 15 mmol, 1.0 equiv). Flask **A** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and THF (30 mL) was then added via syringe. The reaction mixture in flask **A** was then stirred at -78 °C for 15 min. Simultaneously, another 100 mL conical flask (**B**) capped with a rubber septum was charged with sodium hydride (NaH) (654 mg, 27 mmol, 1.8 equiv). Flask **B** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and THF (20 mL) was then added via syringe to form a slurry NaH suspension. The NaH suspension from flask **B** was slowly transferred into flask **A** at -78 °C via syringe, and the reaction mixture in flask **A** was further stirred at -78 °C for 15 min. Benzyl bromide (2.2 mL, 18 mmol, 1.2 equiv) was added into flask **A** via syringe, and the reaction mixture was gradually allowed to warm to room temperature and further stirred overnight. The reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator, and the residue was then washed with water (100 mL) and EtOAc (30 mL). The aqueous layer was further extracted with EtOAc (2 x 30 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using EtOAc / hexanes (1:10) as an eluent to afford 1-benzyl-3-chloro-1*H*-indazole (**S4**) (2.40 g, 9.9 mmol, 66%) as a yellow, low-melting solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.65 (dt, *J* = 8.0 Hz, *J* = 1.2 Hz, 1 H), 7.33 (ddd, *J* = 8.4 Hz, *J* = 6.8 Hz, *J* = 1.2 Hz, 1 H), 7.29-7.18 (ovrlp, 6 H), 7.15 (ddd, *J* = 8.0 Hz, *J* = 6.8 Hz, *J* = 1.2 Hz, 1 H), 5.48 (s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 140.9, 136.3, 133.2, 128.9, 128.0, 127.7, 127.3, 121.5, 121.4, 119.9, 109.7, 53.4. **IR** (neat cm^{-1}) 1616, 1495, 1467, 1336, 1257, 1178, 1005, 764, 728, 693, 651. **HRMS** (ESI) Calcd for $C_{14}H_{11}ClN_2$ [M+H]: 243.0648; Found: 243.0649.



4-Bromo-3-methyl-1-trityl-1*H*-pyrazole (S7). An oven-dried 100 mL round-bottom flask tube equipped with a Teflon-coated magnetic stir bar was charged with 4-bromo-3-methyl-1*H*-pyrazole (860 mg, 5.34 mmol, 1.0 equiv), trityl chloride (2.23 g, 8.01 mmol, 1.5 equiv), triethylamine (2.2 mL, 16.0 mmol, 3 equiv), and chloroform (30 mL). The reaction mixture was then stirred overnight at room temperature. The reaction mixture was washed with hydrochloric acid solution (1 M, ~100 mL) and dichloromethane (~50 mL). The aqueous layer was further extracted with dichloromethane (2 x ~20 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was dissolved with dichloromethane (~10 mL) and then triturated with methanol (~ 50 mL) to give an off-white solid. The solid was filtered and dried *in vacuo* to afford 4-bromo-3-methyl-1-trityl-1*H*-pyrazole (**S8**) (1.58 g, 3.92 mmol, 73%). **m.p.:** 180-181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31-7.29 (ovrlp, 9 H), 7.26 (s, 1 H), 7.15-7.12 (m, 6 H), 2.25 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.9, 143.0, 132.9, 130.2, 127.9, 93.3, 78.9, 12.4. **IR** (neat cm^{-1}) 1488, 1442, 1365, 1128, 1059, 902, 870, 747, 698, 666, 640. **Anal.** Calcd. for $C_{23}H_{19}BrN_2$: C, 68.49; H, 4.75; Found: C, 68.52; H, 4.71.



4-Bromo-3,5-dimethyl-1-trityl-1*H*-pyrazole (**S8**). An oven-dried 100 mL round-bottom flask tube equipped with a Teflon-coated magnetic stir bar was charged with 4-bromo-3,5-dimethyl-1*H*-pyrazole (1.23 g, 7.0 mmol, 1.0 equiv), trityl chloride (2.54 g, 9.1 mmol, 1.3 equiv), potassium *tert*-butoxide (1.18 g, 10.5 mmol, 1.5 equiv), and DMF (20 mL). The reaction mixture was then stirred overnight at room temperature. The reaction mixture was washed with deionized water (~200 mL) and dichloromethane (~50 mL). The aqueous layer was further extracted with dichloromethane (2 x ~20 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was dissolved with dichloromethane (~10 mL) and then triturated with methanol (~50 mL) to give an off-white solid. The solid was filtered and dried *in vacuo* to afford 4-bromo-3,5-dimethyl-1-trityl-1*H*-pyrazole (**S9**) (2.22 g, 5.32 mmol, 71%). **m.p.:** 207-208 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28-7.25 (ovrlp, 9 H), 7.11-7.09 (m, 6 H), 2.19 (s, 3 H), 1.50 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.3, 142.9, 139.5, 130.4, 127.6, 127.4, 97.2, 79.0, 13.9, 13.0. **IR** (neat cm^{-1}) 1492, 1444, 1344, 1227, 1068, 1032, 892, 753, 741, 697. **Anal.** Calcd. for $C_{15}H_{12}N_2O_3$: C, 69.07; H, 5.07; Found: C, 68.90; H, 5.26.



5-chloro-8-methoxyquinoline (**S9**). An oven-dried 250 mL round-bottom flask tube equipped with a Teflon-coated magnetic stir bar was charged with 5-chloro-8-hydroxyquinoline (4.74 g, 26.4 mmol, 1.0 equiv), granulated potassium hydroxide (2.22 g, 39.6 mmol, 1.5 equiv), dimethyl sulfate (9.99 g, 7.5 mL, 79.2 mmol, 3.0 equiv), deionized water (6 mL), and DMF (100 mL). The reaction mixture was then stirred overnight at room temperature. The reaction mixture was washed with deionized water (~200 mL) and EtOAc (~50 mL). The aqueous layer was further extracted with EtOAc (2 x ~20 mL). The combined organic fractions were concentrated *in vacuo* with the aid of a rotary evaporator. The residue was purified by flash column chromatography with silica gel using EtOAc / hexanes (8:1) and then EtOAc as eluents to afford 5-chloro-8-methoxyquinoline (**S9**) (2.79 g, 14.4 mmol, 55%) as an off-white solid. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ: 8.95 (dd, *J* = 4.0 Hz, *J* = 1.6 Hz, 1 H), 8.46 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1 H), 7.50 (dd, *J* = 8.4 Hz, *J* = 4.0 Hz, 1 H), 7.46 (d, *J* = 8.4 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 1 H), 4.05 (s, 3 H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ: 154.4, 149.5, 140.4, 132.7, 126.7, 126.2, 122.2, 121.9, 107.2, 56.0. **HRMS** (ESI) Calcd for $C_{10}H_8ClNO$ [M+H]: 194.0367. Found: 194.0359.

Optimization of Ligand for General Selective Palladium-Catalyzed Arylation of Ammonia (Table 1). An oven-dried 20 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (4.6 mg, 0.005 mmol, 0.010 equiv), ligand (0.025 mmol, 0.050 equiv), and sodium *tert*-butoxide (67.3 mg, 0.70 mmol, 1.4 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). Chlorobenzene (51 μL, 0.50 mmol, 1.0 equiv), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL, 3.0 equiv), and 1,4-dioxane (1.0 mL) were added into the tube via syringe. The reaction mixture was then stirred in an oil bath at 80 ^{o}C for 5 h. After cooling to room temperature, ethyl acetate (~5 mL) and *n*-dodecane (55 μL, 0.25 mmol) were added into the reaction mixture. A small fraction of reaction mixture was filtered through a plug of silica gel and then subjected to GC analysis to determine the reaction conversion and the GC yields of aniline (**1**) and diphenylamine (**2**) using *n*-dodecane as internal standard.

Comparison of the Performance of Palladium Sources on the Arylation of Ammonia (Table S1).

(A) With Pd_2dba_3 without premixing with L6. An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (2.3 mg, 0.0025 mmol, 0.01 equiv), **L6** (5.5 mg, 0.01 mmol, 0.04 equiv), sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (0.25 mmol, 1.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). Ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv), 1,4-dioxane (1.0 mL), and (hetero)aryl halide (if liquid) (0.25 mmol, 1 equiv) were added into the tube via syringe. The tube was then stirred at the required temperature (50 or 80 ^{o}C) in an oil bath for 24 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene

(14.0 mg, 0.083 mmol, 0.33 equiv) were added into the reaction mixture. A portion of the reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator to give crude product. The reaction conversions and the yield of arylamine product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

(B) With Pd_2dba_3 with premixing with L6. An oven-dried 15 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with heteroaryl halide (0.25 mmol, 1.0 equiv) and sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv). Tube **A** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv) was then added into the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (2.3 mg, 0.0025 mmol, 0.01 equiv) and **L6** (5.5 mg, 0.01 mmol, 0.04 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (1.0 mL) was then added into the tube. The reaction mixture in tube **B** was stirred at 100 ^oC in an oil bath for 3 min, after which time the color of the reaction mixture changed from deep purple to deep brown, indicating the formation of Pd-**L6** catalyst. After cooling to room temperature, the solution of Pd-**L6** from tube **B** was transferred into tube **A** via syringe. The reaction mixture in tube **A** was stirred in an oil bath at 50 ^oC for 24 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.33 equiv) were added into the reaction mixture. A portion of the reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator to give crude product. The reaction conversion and the yield of arylamine products were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

(C) With Pd precatalyst 3a. An oven-dried 15 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with **L6** (5.5 mg, 0.005 mmol, 0.02 equiv), sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (0.25 mmol, 1 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv) and (hetero)aryl halide (if liquid) (0.25 mmol, 1.0 equiv) were then added into the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with **3a** (4.6 mg, 0.005 mmol, 0.02 equiv), and the tube was evacuated and backfilled with argon (this sequence was repeated a total of three times). 1,4-Dioxane (1.0 mL) was added into tube **B** via syringe, and the reaction mixture was then stirred at room temperature for ~1 min to form a homogeneous solution. The solution of **3a** from tube **B** was then transferred into tube **A** via syringe. The reaction mixture in tube **A** was then stirred at the required temperature (50 or 80 ^oC) in an oil bath for 24 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.33 equiv) were added into the reaction mixture. A portion of the reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator to give crude product. The conversion and the yield of arylamine product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Optimization of Ligand for Selective Palladium-Catalyzed Coupling of Ammonia with Sterically Hindered (Hetero)aryl Halides (Scheme S1). An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (2.3 mg, 0.0025 mmol, 0.01 equiv), ligand (**L6** or **L7**; 0.01 mmol, 0.04 equiv), and sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv), (and 5-chloro-8-methoxyquinoline as a solid (48.4 mg, 0.25 mmol, 1 equiv)). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). Ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv) and 1,4-dioxane (1.0 mL) (and 2-chloro-1,3-xylene as a liquid (33 μL, 0.25 mmol, 1.0 equiv)) were added into the tube via syringe. The reaction mixture was then stirred in an oil bath at 100 ^{o}C for 24 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.33 equiv) were added into the reaction mixture. A portion of the reaction mixture was dried *in vacuo* with the aid of a rotary evaporator to give crude product. The yield of arylamine product and diarylamine side-product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

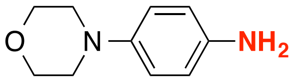
Optimization of Ligand for Selective Palladium-Catalyzed Coupling of Ammonia with Five-Membered Heteroaryl Halides (Scheme S1). An oven-dried 15 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with 1-(4-fluorophenyl)-4-bromopyrazole (60.3 mg, 0.25 mmol, 1.0 equiv) and sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv) was then added into tube **A** via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (2.3 mg, 0.0025 mmol, 0.01 equiv) and ligand (**L3**, **L4**, or **L6**; 0.01 mmol, 0.04 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (1.0 mL) was then added into tube **B** via syringe. The reaction mixture in tube **B** was stirred at 100 ^{o}C in an oil bath for 3 min, after which time the color of the reaction mixture changed from dark purple to deep brown, indicating the formation of Pd-**L** catalyst. After cooling to room temperature, the deep brown Pd-**L** solution from tube **B** was transferred into tube **A** via syringe. The reaction mixture in tube **A** was then stirred in an oil bath at 120 ^{o}C for 20 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.033 mmol) were added into the reaction mixture. A portion of the reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator to give crude product. The reaction conversion and the yield of arylamine product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Substrate Scope for the Selective Palladium-Catalyzed Arylation of Ammonia for the Synthesis of Arylamines (Schemes 2-5).

General Procedure A (For General Use): An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with **L6** (11.0 mg, 0.020 mmol, 0.020 equiv), sodium *tert*-butoxide (134.5 mg, 1.4 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (1.0 mmol, 1.0 equiv). Tube **A** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 6.0 mL, 3.0 mmol, 3.0 equiv) and (hetero)aryl halide (if liquid) (1.0 mmol, 1.0 equiv) were then added into the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd precatalyst **3a** (18.4 mg, 0.020 mmol, 0.020 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (4.0 mL) was added into the tube via syringe. The reaction mixture in tube **B** was stirred at room temperature for ~1 min to form a homogeneous solution. The solution of **3a** from tube **B** was then transferred into tube **A** via syringe. The reaction mixture in tube **A** was stirred at an elevated temperature in an oil bath for 24 h. After cooling to room temperature, the crude product was diluted with ethyl acetate (~20 mL) and concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel or alumina using a solvent mixture (ethyl acetate (EtOAc), hexanes, and/or methanol (MeOH)) as an eluent to afford the isolated arylamine product. The reported yields are of isolated products and averages of two runs.

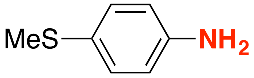
General Procedure B (For Sterically Hindered (Hetero)aryl Halides): An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with **L7** (10.7 mg, 0.02 mmol, 0.020 equiv), sodium *tert*-butoxide (134.5 mg, 1.4 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (1.0 mmol, 1.0 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 6.0 mL, 3.0 mmol, 3.0 equiv) and (hetero)aryl halide (if liquid) (1.0 mmol, 1.0 equiv) were then added in the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd precatalyst **3b** (18.1 mg, 0.020 mmol, 0.020 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (4.0 mL) was added into the tube via syringe. The reaction mixture in tube **B** was stirred at room temperature for ~1 min to form a homogeneous solution. The solution of **3b** from tube **B** was then transferred into tube **A** via syringe. The reaction mixture in tube **A** was stirred at an elevated temperature in an oil bath for 24 h. After cooling to room temperature, the crude product was diluted with ethyl acetate (~ 20 mL) and concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was purified by flash column chromatography with silica gel or alumina using a solvent mixture (ethyl acetate (EtOAc), hexanes, and/or methanol (MeOH)) as an eluent to afford the isolated arylamine product. The reported yields are of isolated products and averages of two runs.

General Procedure C (For Five-Membered Heteroaryl Halides): An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with **L4** (12.8 mg, 0.020 mmol, 0.020 equiv), sodium *tert*-butoxide (134.5 mg, 1.4 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (1.0 mmol, 1.0 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 6.0 mL, 3.0 mmol, 3.0 equiv) and (hetero)aryl halide (if liquid) (1.0 mmol, 1.0 equiv) were then added into the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) was charged with Pd precatalyst **3c** (20.2 mg, 0.02 mmol, 0.02 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (4.0 mL) was then added into the tube via syringe. The reaction mixture in tube **B** was shaken with the aid of an ultrasonic water-bath at room temperature until all **3c** dissolved to form a clear solution. The solution of **3c** from tube **B** was then transferred into tube **A** via syringe. The reaction mixture in tube **A** was stirred at an elevated temperature in an oil bath for 20-24 h. After cooling to room temperature, the crude product was diluted with ethyl acetate (~20 mL) and concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was then purified by flash column chromatography with silica gel or alumina using a solvent mixture (ethyl acetate (EtOAc), hexanes, and/or methanol (MeOH)) as an eluent to afford the isolated arylamine product. The reported yields are of isolated products and averages of two runs.



4-Morpholinoaniline (4a).[12] Following the general procedure A, the title compound was prepared using 4-(4-chlorophenyl)morpholine (197.7 mg, 1.0 mmol), Pd precatalyst **3a** (23.0 mg, 0.025 mmol), and **L6** (13.7 mg, 0.025 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc as an eluent to afford an inseparable brown solid mixture of 4-

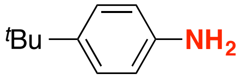
morpholinoaniline (**4a**) (143 mg, 0.80 mmol, 80%) and bis(4-morpholinophenyl)amine (**4a'**) (4%) The 1^{o} : 2^{o} ratio was determined to be 22 : 1 in the isolated product mixture. **^{1}H NMR** (**1^{o}**) (400 MHz, CDCl$_3$) δ: 6.77 (d, J = 8.8 Hz, 2 H), 6.62 (d, J = 8.4 Hz, 2 H), 3.82 (t, J = 4.8 Hz, 4 H), 3.46 (br s, 2 H), 2.99 (t, J = 4.8 Hz, 4 H). **^{13}C NMR** (**1^{o}**) (100 MHz, CDCl$_3$) δ: 144.4, 140.4, 118.2, 116.3, 67.1, 51.1. **IR** (neat cm^{-1}) 3382, 3325, 3223, 2854, 1642, 1511, 1447, 1260, 1227, 1167, 1107, 1061, 916, 827, 765, 718. **HRMS** (ESI) Calcd for $C_{10}H_{14}N_2O$ [M+H] (**1^{o}**): 179.1179; Found: 179.1174; Calcd for $C_{20}H_{25}N_3O_2$ [M+H] (**2^{o}**): 340.2020; Found: 340.2042.



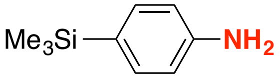
4-(Methylthio)aniline (4b).[13]

(i) 50 °C. Following the general procedure A, the title compound was prepared using 1-chloro-4-(methylthio)benzene (158.7 mg, 130 μL 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) as an eluent to afford 4-(methylthio)aniline (**4b**) (130.3 mg, 0.94 mmol, 94%) as a brown oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 7.14 (d, J = 7.2 Hz, 2 H), 6.56 (d, J = 7.2 Hz, 2 H), 3.65 (br s, 2 H), 2.37 (s, 3 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 145.1, 130.8, 125.4, 115.6, 18.6. **IR** (neat cm^{-1}) 3345, 1618, 1597, 1494, 1422, 1275, 967, 817, 683. **Anal.** Calcd. for C_7H_9NS: C, 60.39; H, 6.52; Found: C, 60.38; H, 6.62.

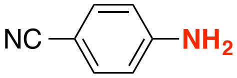
(ii) rt. Following the general procedure A, the title compound was prepared using 1-bromo-4-(methylthio)benzene (101.6 mg, 0.50 mmol) **3a** (23.0 mg, 0.025 mmol, 5 mol %), **L6** (13.7 mg, 0.025 mmol, 5 mol %), NaO^{t}Bu (67.3 mg, 0.70 mmol), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL), and 1,4-dioxane (0.50 mL) at room temperature for 36 h. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) an as eluent to afford 4-(methylthio)aniline (**4b**) (56.6 mg, 0.41 mmol, 81%) as a brown oil. The reaction conversion was determined to be ~80% by ^{1}H NMR spectroscopy of the crude reaction mixture. Spectral and analytical data were identical to those reported for the same compound above.



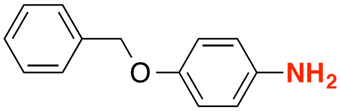
4-(*tert*-Butyl)aniline (4c).[14] Following the general procedure A, the title compound was prepared using 1-(*tert*-butyl)-4-chlorobenzene (168.7 mg, 167 μL, 1.0 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) as an eluent to afford 4-(*tert*-butyl)aniline (**4c**) (126.8 mg, 0.85 mmol, 85%) as a brown oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 7.16 (d, J = 8.0 Hz, 2 H), 6.60 (d, J = 8.0 Hz, 2 H), 3.49 (br s, 2 H), 1.27 (s, 9 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 143.9, 141.3, 126.1, 115.0, 33.9, 31.6. **IR** (neat cm^{-1}) 3350, 2957, 2903, 2866, 1623, 1515, 1363, 1265, 1189, 825, 643. **HRMS** (ESI) Calcd for $C_{10}H_{15}N$ [M+H]: 150.1277; Found: 150.1286.



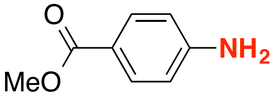
4-(Trimethylsilyl)aniline (4d).[15] Following the general procedure A, the title compound was prepared using (4-chlorophenyl)trimethylsilane (184.7 mg, 186 μL 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:4) as an eluent to afford 4-(trimethylsilyl)aniline (**4d**) (151.5 mg, 0.92 mmol, 92%) as a brown oil. **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 7.30 (d, J = 8.4 Hz, 2 H), 6.66 (d, J = 8.0 Hz, 2 H), 3.65 (br s, 2 H), 0.22 (s, 9 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 147.2, 134.7, 128.4, 114.7, -0.77. **IR** (neat cm^{-1}) 3375, 2953, 1597, 1498, 1617, 1247, 1111, 898, 835, 713. **HRMS** (ESI) Calcd for $C_9H_{15}NSi$ [M+H]: 166.1047; Found: 166.1049.



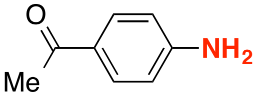
4-Aminobenzonitrile (4e).[13] Following the general procedure A, the title compound was prepared using 4-chlorobenzonitrile (137.6 mg, 1.0 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:1) as an eluent to afford 4-aminobenzonitrile (**4e**) (86.7 mg, 0.74 mmol, 74%) as a pale-brown solid. **m.p.**: 82-84 °C (lit: 82-84 °C).[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 2 H), 6.64 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 2 H), 4.36 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 150.8, 133.7, 120.4, 114.3, 99.3. **IR** (neat cm^{-1}) 3447, 3344, 2220, 1629, 1599, 1512, 1310, 1171, 830, 699. **HRMS** (ESI) Calcd for $C_7H_6N_2$ [M+H]: 119.0604; Found: 119.0605.



4-(Benzyloxy)aniline (4f).[17] Following the general procedure A, the title compound was prepared using 1-(benzyloxy)-4-bromobenzene (131.6 mg, 0.50 mmol) **3a** (23.0 mg, 0.025 mmol, 5 mol %), **L6** (13.7 mg, 0.025 mmol, 5 mol %), NaO^{t}Bu (67.3 mg, 0.70 mmol), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL), and 1,4-dioxane (0.50 mL) at room temperature for 36 hours. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) and then EtOAc / hexanes (2:1) as eluents to afford 4-(benzyloxy)aniline (**4b**) (83.5 mg, 0.84 mmol, 84%) as a deep-brown solid. The reaction conversion was determined to be ~90% by ^{1}H NMR spectroscopy of the crude reaction mixture. **m.p.:** 41-42 °C (lit: 45-46.5 °C).[17] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 7.2 Hz, 2 H), 7.35 (t, *J* = 7.2 Hz, 2 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 4.96 (s, 2 H), 3.37 (s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.0, 140.3, 137.6, 128.6, 127.9, 127.6, 116.4, 116.1, 70.8. **IR** (neat cm^{-1}) 3354, 3032, 1623, 1508, 1453, 1380, 1265, 1227, 1016, 822, 733, 696. **HRMS** (ESI) Calcd for $C_{13}H_{13}NO$ [M+H]: 200.1070; Found: 200.1076.

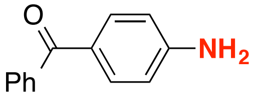


Methyl 4-Aminobenzoate (4g).[13] Following the general procedure A, the title compound was prepared using methyl 4-chlorobenzoate (170.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) as an eluent to afford methyl 4-aminobenzoate (**4g**) (80.6 mg, 0.53 mmol, 53%) as an off-white solid. **m.p.:** 109 °C (lit: 112-113 °C).[16] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.0 Hz, 2 H), 6.62 (d, *J* = 8.0 Hz, 2 H), 4.16 (br s, 2 H), 3.84 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.3, 151.1, 131.6, 119.5, 113.8, 51.6. **IR** (neat cm^{-1}) 3405, 3336, 3230, 2, 1635, 1597, 1515, 1434, 1313, 1283, 1176, 1118, 768, 698. **Anal.** Calcd. for $C_8H_9NO_2$: C, 63.56; H, 6.00; Found: C, 63.48; H, 6.02.



4'-Aminoacetophenone (4h).[13] Following the general procedure A, the title compound was prepared using 4'-chloroacetophenone (154.6 mg, 130 μL 1.0 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:1) as an eluent to afford 4'-aminoacetophenone (**4h**) (81.3 mg, 0.60 mmol, 60%) as a pale-yellow solid. **m.p.:** 104-106 °C (lit:

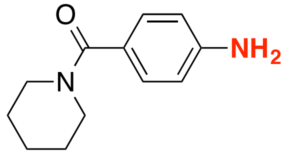
103-107 °C).[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.4 Hz, 2 H), 6.63 (d, *J* = 8.8 Hz, 2 H), 4.31 (br s, 2 H), 2.49 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 196.7, 151.5, 130.8, 127.6, 113.7, 26.1. **IR** (neat cm^{-1}) 3388, 3325, 3221, 1650, 1637, 1585, 1564, 1514, 1436, 1359, 1304, 1279, 1177, 960, 836, 819. **Anal.** Calcd. for C_8H_9NO: C, 71.09; H, 6.71; Found: C, 70.94; H, 6.78.



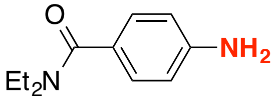
4-Aminobenzophenone (4i).[13]

(i) 50 °C. Following the general procedure A, the title compound was prepared using 4-chlorobenzophenone (216.7 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:1) as an eluent to afford 4-aminobenzophenone (**4i**) (184.0 mg, 0.93 mmol, 93%) as a pale-yellow solid. **m.p.:** 122-123 °C (lit.: 121-124 °C).[18] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.71-7.67 (ovrlp, 4 H), 7.50 (t *J* = 7.6 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 2 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 4.37 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 195.4, 151.5, 138.9, 132.9, 131.4, 129.4, 128.1, 126.9, 113.6. **IR** (neat cm^{-1}) 3417, 3335, 3221, 1627, 1585, 1441, 1319, 1285, 1150, 937, 922, 794, 844, 756. **Anal.** Calcd. for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; Found: C, 79.08; H, 5.70.

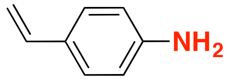
(ii) rt. Following the general procedure A, the title compound was prepared using 4-bromobenzophenone (130.6 mg, 0.50 mmol), **3a** (23.0 mg, 0.025 mmol, 5 mol %), **L6** (13.7 mg, 0.025 mmol, 5 mol %), NaO^{t}Bu (67.3 mg, 0.70 mmol), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL), and 1,4-dioxane (0.50 mL) at room temperature for 36 hours. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) as an eluent to afford 4-aminobenzophenone (**4i**) (98.6 mg, 0.48 mmol, 96%) as a pale-yellow solid. Spectral and analytical data were identical to those reported for the same compound above.



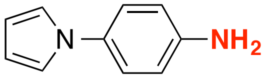
(4-Aminophenyl)(piperidin-1-yl)methanone (4j).[19] Following the general procedure A, the title compound was prepared using (4-chlorophenyl)(piperidin-1-yl)methanone (223.7 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc as an eluent to afford (4-aminophenyl)(piperidin-1-yl)methanone (**4j**) (178.6 mg, 0.88 mmol, 88%) as an off-white solid. **m.p.:** 161-163 °C (lit.: 160 °C).[19] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.4 Hz, 2 H), 6.59 (d, *J* = 8.4 Hz, 2 H), 4.04 (br s, 2 H), 3.54 (br s, 4 H), 1.67-1.63 (m, 2 H), 1.57 (br s, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.7, 148.3, 128.8, 125.1, 113.9, 25.9, 24.5. **IR** (neat cm^{-1}) 3453, 3308, 3201, 2938, 1630, 1588, 1565, 1428, 1291, 1276, 1000, 845, 762. **Anal.** Calcd. for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; Found: C, 70.28; H, 7.84.



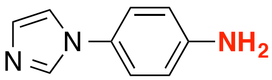
4-Amino-*N*,*N*-diethylbenzamide (4k).[20] Following the general procedure A, the title compound was prepared using 4-bromo-*N*,*N*-diethylbenzamide (128.1 mg, 0.50 mmol) **3a** (23.0 mg, 0.025 mmol, 5 mol %), **L6** (13.7 mg, 0.025 mmol, 5 mol %), NaO^{t}Bu (67.3 mg, 0.70 mmol), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL), and 1,4-dioxane (0.50 mL) at room temperature for 36 h. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) and then EtOAc as eluents to afford 4-amino-*N*,*N*-diethylbenzamide (**4k**) (90.0 mg, 0.47 mmol, 94%) as a pale-yellow solid. **m.p.**: 123-124 °C (lit.: 118-120 °C)[20] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.19 (d, *J* = 8.4 Hz, 2 H), 6.61 (d, *J* = 8.4 Hz, 2 H), 3.91 (br s, 2 H), 3.41 (br s, 4 H), 1.17 (t, *J* = 7.2 Hz, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.8, 147.8, 128.2, 126.7, 114.2, 13.6. **IR** (neat cm^{-1}) 3434, 3333, 2973, 1629, 1595, 1568, 1522, 1424, 1382, 1286, 1176, 1099, 836, 764. **HRMS** (ESI) Calcd for $C_{11}H_{16}N_2O$ [M+H]: 193.1335; Found: 193.1343.



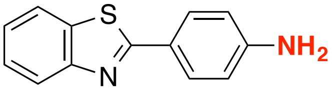
4-Vinylaniline (4l).[21] Following the general procedure A, the title compound was prepared using 1-chloro-4-vinylbenzene (138.6 mg, 126 μL, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:4) as an eluent to afford 4-vinylaniline (**4l**) (69.6 mg, 0.58 mmol, 58%) as a brown oil. A trace amount of bis(4-vinylphenyl)amine (**4l'**) formed as detected by GC/MS analysis of the crude reaction mixture based on 0.25 mmol aryl halide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.4 Hz, 2 H), 6.64-6.57 (ovrlp, 3 H), 5.53 (d, *J* = 17.6 Hz, 1 H), 5.03 (d, *J* = 10.8 Hz, 1 H), 3.66 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 146.3, 136.6, 128.4, 127.4, 115.1, 110.1. **IR** (neat cm^{-1}) 3355, 1606, 1513, 1316, 1279, 1177, 989, 891, 824. **HRMS** (ESI) Calcd for C_8H_9N [M+H]: 120.0808; Found: 120.0809.



4-(1*H*-Pyrrol-1-yl)aniline (4m).[22] Following the general procedure A, the title compound was prepared using 1-(4-chlorophenyl)-1*H*-pyrrole (177.6 mg, 1.0 mmol), Pd precatalyst **3a** (6.4 mg, 0.007 mmol), **L6** (3.8 mg, 0.007 mmol), and 1,4-dioxane (6.0 mL) at 110 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:6) and then EtOAc / hexanes (1:2) as eluents to afford 4-(1*H*-pyrrol-1-yl)aniline (**4m**) (142.6 mg, 0.90 mmol, 90%) as a pale-yellow solid. The 1° : 2° ratio was determined to be 9 : 1 in the crude product based on 0.25 mmol aryl halide. **m.p.:** 80 °C (**lit:** 86-87 °C).[22] **^{1}H NMR** (400 MHz, $CDCl_3$) δ:) δ: 7.12 (d, *J* = 8.4 Hz, 2 H), 6.94 (t, *J* = 2.0 Hz, 2 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.29 (t, *J* = 2.0 Hz, 2 H), 3.58 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.6, 132.8, 122.3, 119.7, 115.6, 109.5. **IR** (neat cm^{-1}) 3416, 3331, 3219, 1626, 1518, 1320, 1277, 1256, 1128, 1078, 1020, 922, 822, 721, 641. **Anal.** Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; Found: C, 75.86; H, 6.51.



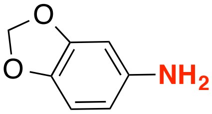
4-(1*H*-imidazol-1-yl)aniline (4n).[23] Following the general procedure A, the title compound was prepared using 1-(4-chlorophenyl)-1*H*-imidazole (178.6 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with alumina using EtOAc (100%) and then EtOAc / MeOH (15:1) as eluents to afford 4-(1*H*-imidazol-1-yl)aniline (**4n**) (132.9 mg, 0.83 mmol, 83%) as a pale-yellow solid. **m.p.:** 143-144 °C (lit: 145-146 °C).[24] **^{1}H NMR** (400 MHz, $CDCl_3$ δ: 7.72 (s, 1 H), 7.16 (ovrlp, 2 H), 7.13 (d, *J* = 8.8 Hz, 2 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 3.94 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 146.3, 135.9, 129.7, 128.6, 123.3, 118.9, 115.5. **IR** (neat cm^{-1}) 3342, 3184, 3114, 1609, 1519, 1282, 1254, 1103, 1059, 909, 827, 741, 699, 663. **HRMS** (ESI) Calcd for $C_9H_9N_3$ [M+H]: 160.0869; Found: 160.0859.



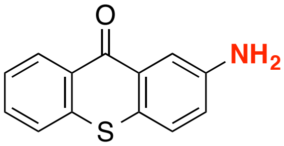
4-(benzothiazol-2-yl)aniline (4o).[25]

(i) 50 °C. Following the general procedure A, the title compound was prepared using 2-(4-chlorophenyl)benzothiazole (245.7 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) and then EtOAc / hexanes (1:1) as eluents to afford 4-(benzothiazol-2-yl)aniline (**4o**) (197.5 mg, 0.87 mmol, 87%) as a pale-yellow solid. **m.p.:** 155-156 °C (lit: 156-157 °C).[25] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.99 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.43 (t, *J* = 8.0 Hz, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 6.71 (d, *J* = 8.4 Hz, 2 H), 4.01 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 168.6, 154.3, 149.4, 134.7, 129.2, 126.2, 124.5, 123.9, 122.5, 121.5, 114.8. **IR** (neat cm^{-1}) 3450, 3292, 3184, 1627, 1604, 1471, 1432, 1309, 1228, 1178, 965, 826, 756, 728, 699. **HRMS** (ESI) Calcd for $C_{13}H_{10}N_2S$ [M+H]: 227.0637; Found: 227.0621.

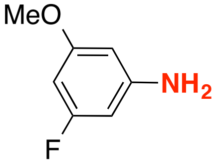
(ii) rt. Following the general procedure A, the title compound was prepared using 2-(4-chlorophenyl)benzothiazole (122.9 mg, 0.50 mmol), **3a** (13.8 mg, 0.015 mmol, 3 mol %), **L6** (8.2 mg, 0.015 mmol, 3 mol %), NaO^{t}Bu (67.3 mg, 0.70 mmol), ammonia solution (0.5 M in 1,4-dioxane, 3.0 mL), and 1,4-dioxane (0.50 mL) at room temperature. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) and then EtOAc / hexanes (1:1) as eluents to afford 4-(benzothiazol-2-yl)aniline (110.3 mg, 0.49 mmol, 97%) as a pale-yellow solid. Spectral and analytical data were identical to those reported for the same compound above.



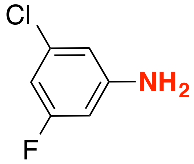
5-Aminobenzo[1,3]dioxole (4p).[1] Following the general procedure A, the title compound was prepared using 5-chlorobenzo[*d*][1,3]dioxole (156.6 mg, 117 μL, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:2) as an eluent to afford 5-aminobenzo[1,3]dioxole (**4p**) (113.2 mg, 0.83 mmol, 83%) as a low-melting, deep-brown solid. The 1° : 2° ratio was determined to be 13 : 1 in the crude product based on 0.25 mmol aryl halide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.60 (d, *J* = 8.0 Hz, 1 H), 6.26 (d, *J* = 2.0 Hz, 1 H), 6.09 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1 H), 5.82 (s, 2 H), 3.47 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.2, 141.5, 140.2, 108.6, 106.8, 100.6, 98.0. **IR** (neat cm^{-1}) 3420, 3309, 3207, 2900, 1635, 1609, 1486, 1458, 1265, 1191, 1108, 1030, 942, 925, 831, 795, 667. **Anal.** Calcd. for $C_{15}H_{12}N_2O_3$: C, 61.31; H, 5.14; Found: Found: C, 61.61; H, 5.22.



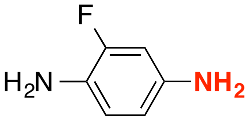
2-amino-9*H*-thioxanthen-9-one (4q).[26] Following the general procedure A, the title compound was prepared using 2-chloro-9*H*-thioxanthen-9-one (246.7 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) and then EtOAc / hexanes (1:2) as eluents to afford 2-amino-9*H*-thioxanthen-9-one (**4q**) (182.2 mg, 0.80 mmol, 80%) as a sunset-yellow solid. **m.p.:** 226-228 °C (lit: 227-228 °C).[26] **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ: 8.44 (d, *J* = 8.0 Hz, 1 H), 7.74-7.65 (ovrlp, 3 H), 7.51-7.47 (ovrlp, 2 H), 7.10 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1 H), 5.69 (br s, 2 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 178.7, 148.1, 137.2, 132.2, 129.4, 129.1, 127.9, 127.1, 126.4, 125.9, 122.1, 121.2, 110.9. **IR** (neat cm^{-1}) 3425, 3339, 1616, 1587, 1481, 1436, 1323, 1166, 820, 733. **Anal.** Calcd. for $C_{13}H_9NOS$: C, 68.70; H, 3.99; Found: C, 68.76; H, 4.21.



3-Fluoro-5-methoxyaniline (4r).[1] Following the general procedure A, the title compound was prepared using 1-chloro-3-fluoro-5-methoxybenzene (160.6 mg, 127 μL, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:3) as an eluent to afford 3-fluoro-5-methoxyaniline (**4r**) (113.4 mg, 0.80 mmol, 80%) as a brown oil. The 1° : 2° ratio was determined to be 26 : 1 in the crude product based on 0.25 mmol aryl halide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.03 (dt, $^{3}J_{HF}$ = 10.8 Hz, $^{3}J_{HH}$ = 2.4 Hz, 1 H), 6.00-5.96 (ovrlp, 2 H), 2.77 (br s, 2 H), 3.71 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.6 (d, $^{1}J_{CF}$ = 239.9 Hz), 161.8 (d, $^{3}J_{CF}$ = 13.6 Hz), 148.8 (d, $^{3}J_{CF}$ = 13.5 Hz), 96.6 (d, $^{4}J_{CF}$ = 2.2 Hz), 94.9 (d, $^{2}J_{CF}$ = 25.0 Hz), 91.8 (d, $^{2}J_{CF}$ = 25.5 Hz), 55.4. **IR** (neat cm^{-1}) 3465, 3377, 1616, 1588, 1476, 1197, 1164, 1128, 1047, 1004, 943, 818, 675. **Anal.** Calcd. for C_7H_8FNO: C, 59.57; H, 5.71; Found: C, 59.80; H, 5.83.

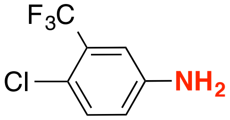


3-Chloro-5-fluoroaniline (4s). Following the general procedure A, the title compound was prepared using 1-bromo-3-chloro-5-fluorobenzene (209.4 mg, 122 μL, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:5) and then EtOAc / hexanes (1:3) as eluents to afford 3-fluoro-5-methoxyaniline (**4s**) (76.2 mg, 0.52 mmol, 52%) as a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.45 (d, $^{3}J_{HF}$ = 8.8 Hz, 1 H), 6.42 (s, 1 H), 6.24 (d, $^{3}J_{HF}$ = 10.4 Hz, 1 H), 3.83 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 163.7 (d, $^{1}J_{CF}$ = 244.4 Hz), 148.8 (d, $^{3}J_{CF}$ = 12.1 Hz), 135.5 (d, $^{3}J_{CF}$ = 13.3 Hz), 110.9 (d, $^{4}J_{CF}$ = 2.7 Hz), 106.0 (d, $^{2}J_{CF}$ = 25.2 Hz), 100.4 (d, $^{2}J_{CF}$ = 24.6 Hz). **IR** (neat cm^{-1}) 3377, 2927, 2854, 1712, 1601, 1584, 1462, 1273, 1153, 874, 834, 713. **HRMS** (ESI) Calcd for C_6H_5ClFN [M+H]: 146.0167; Found: 146.0185.

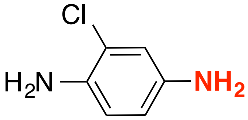


2-Fluorobenzene-1,4-diamine (4t).[27] Following the general procedure A, the title compound was prepared using 4-chloro-2-fluoroaniline (145.6, 111 μL, 1.0 mmol) and NaO^{t}Bu (211.4 mg, 2.2 mmol, 2.2 equiv) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (4:1) as an eluent to afford 2-fluorobenzene-1,4-diamine (**4t**) (84.8 mg, 0.67 mmol, 67%) as a reddish-brown solid. The 1° : 2° ratio was determined to be 20 : 1 in the crude product based on 0.25 mmol aryl halide. **m.p.:** 87-88 °C (lit: 88-89 °C).[25] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.61 (dd, $^{4}J_{HF}$ = 9.6 Hz, $^{3}J_{HH}$ = 8.8 Hz, 1 H), 6.40 (dd, $^{3}J_{HF}$ = 12.4 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1 H), 6.31 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1 H), 3.37 (br ovrlp, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 152.6 (d, $^{1}J_{CF}$ = 236.5 Hz), 139.4 (d, $^{3}J_{CF}$ = 9.2 Hz), 126.02 (d, $^{2}J_{CF}$ = 13.5 Hz), 118.5 (d, $^{3}J_{CF}$ = 4.7 Hz), 111.5 (d, $^{4}J_{CF}$ = 3.1

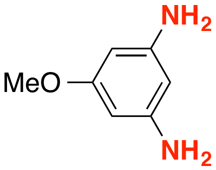
Hz), 103.6 (d, $^{2}J_{CF}$ = 21.96 Hz). **IR** (neat cm^{-1}) 3400, 3307, 3203, 1623, 1591, 1516, 1459, 1299, 1237, 1147, 953, 834, 746, 667. **HRMS** (ESI) Calcd for $C_6H_7FN_2$ [M+H]: 127.0666; Found: 127.0667.



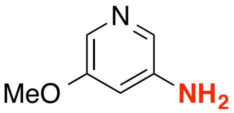
4-Chloro-3-(trifluoromethyl)aniline (4u).[28] Following the general procedure A, the title compound was prepared using 4-bromo-1-chloro-2-(trifluoromethyl)benzene (259.5 mg, 149 μL, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:8) and then EtOAc / hexanes (1:5) as eluents to afford 4-chloro-3-(trifluoromethyl)aniline (**4u**) (140.9 mg, 0.72 mmol, 72%) as a brown solid. The 1° : 2° ratio was determined to be 19 : 1 in the crude product based on 0.25 mmol aryl halide. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.20 (d, J = 8.4 Hz, 1 H), 6.94 (d, J = 2.4 Hz, 1 H), 6.70 (dd, J = 8.4 Hz, J = 2.4 Hz, 1 H), 3.84 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 145.3, 132.2, 128.7 (q, $^{2}J_{CF}$ = 30.8 Hz), 123.0 (q, $^{1}J_{CF}$ = 271.5 Hz), 120.2 (q, $^{3}J_{CF}$ = 1.7 Hz), 118.8, 113.7 (q, $^{3}J_{CF}$ = 5.4 Hz). **IR** (neat cm^{-1}) 3383, 1626, 1485, 1444, 1334, 1256, 1169, 1114, 1028, 869, 821, 668. **HRMS** (ESI) Calcd for $C_7H_5ClF_3N$ [M+H]: 196.0135; Found: 196.0136.



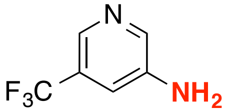
2-Chlorobenzene-1,4-diamine (4v).[29] Following the general procedure A, the title compound was prepared using 4-bromo-2-chloroniline (206.5 mg, 1.0 mmol) and NaO^{t}Bu (211.4 mg, 2.2 mmol, 2.2 equiv) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc / hexanes (1:1) and then EtOAc / hexanes (2:1) as eluents to afford 2-chlorobenzene-1,4-diamine (**4v**) (112.6 mg, 0.79 mmol, 79%) as a deep brown solid. **m.p.:** 61-62 °C (lit: 62-64 °C).[30] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.64 (d, J = 2.8 Hz, 1 H), 6.60 (d, J = 8.4 Hz, 1 H), 6.46 (dd, J = 8.4 Hz, J = 2.8 Hz, 1 H), 3.51 (br ovrlp, 4 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 139.1, 135.2, 120.4, 117.4, 116.4, 115.6. **IR** (neat cm^{-1}) 3411, 3322, 1602, 1500, 1435, 1303, 1234, 1038, 862, 814, 711, 667. **HRMS** (ESI) Calcd for $C_6H_7ClN_2$ [M+H]: 143.0371; Found: 143.0371.



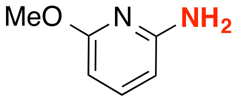
5-Methoxybenzene-1,3-diamine (4w). Following the general procedure A, the title compound was prepared using 1,3-dichloro-5-methoxybenzene (177.0 mg, 1.0 mmol), NaO^{t}Bu (269.1 mg, 2.8 mmol, 2.8 equiv), ammonia solution (0.5 M, 12.0 mL, 6.0 mmol, 6.0 equiv), and 1,4-dioxane (1.0 mL) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc as an eluent to afford an inseparable viscous deep brown oily mixture of 5-methoxybenzene-1,3-diamine (**4w**) (108 mg, 0.78 mmol, 78%) and 3,3'-diamino-5,5'-dimethoxy-diphenylamine (**4w'**) (9%). The 1° : 2° ratio was determined to be 9 : 1 in the isolated product mixture. **^{1}H NMR (1°)** (400 MHz, $CDCl_3$) δ: 5.68 (s, 2 H), 5.61 (s, 1 H), 3.68 (s, 3 H), 3.58 (br s, 4 H). **^{13}C NMR (1°)** (100 MHz, $CDCl_3$) δ: 161.7, 148.6, 95.1, 91.9, 55.0. **HRMS** (ESI) Calcd for $C_7H_{10}N_2O$ [M+H] (**1°**): 139.0866. Found: 139.0857; Calcd for $C_{14}H_{17}N_3O_2$ [M+H] (**2°**): 260.1394. Found: 260.1403.



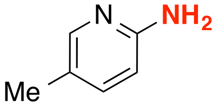
3-Amino-5-methoxypyridine (5a).[31] Following the general procedure A, the title compound was prepared using 3-bromo-5-methoxypyridine (188.0 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/Et_3N (50:1) using EtOAc and then EtOAc/MeOH (15:1) as eluents to afford an inseparable brown solid mixture of 3-amino-5-methoxypyridine (**5a**) (113 mg, 0.91 mmol, 91%) and bis(5-methoxypyridin-3-yl)amine (**5a'**) (4%) The 1° : 2° ratio was determined to be 23 : 1 the isolated product mixture. **^{1}H NMR (1°)** (400 MHz, $CDCl_3$) δ: 7.72-7.71 (ovrlp, 2 H), 6.52 (t, J = 2.4 Hz, 1 H), 4.04 (br s, 2 H), 3.79 (s, 3 H). **^{13}C NMR (1°)** (100 MHz, $CDCl_3$) δ: 156.4, 143.9, 129.9, 126.9, 106.7, 55.3. **IR** (neat cm^{-1}) 3335, 3152, 1588, 1486, 1446, 1430, 1332, 1270, 1204, 1173, 1039, 1017, 969, 843, 734, 700. **HRMS** (ESI) Calcd for $C_6H_8N_2O$ [M+H] (**1°**): 125.0709. Found: 125.0709; Calcd for $C_{12}H_{13}N_3O_2$ [M+H]: (**2°**): 232.1081. Found: 232.1090.



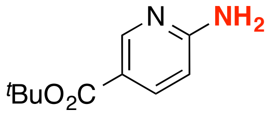
3-Amino-5-(trifluoromethyl)pyridine (5b).[32] Following the general procedure A, the title compound was prepared using 3-chloro-5-(trifluoromethyl)pyridine (181.5 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) and then EtOAc/hexanes (2:1) as eluents to afford an inseparable brown oily mixture of 3-amino-5-(trifluoromethyl)pyridine (**5b**) (147.5 mg, 0.94 mmol, 94%) and bis(5-(trifluoromethyl)pyridin-3-yl)amine (**5b'**) (2%). The 1° : 2° ratio was determined to be 47 : 1 of the isolated product mixture based on 0.25 mmol heteroaryl halide. **^{1}H NMR (1°)** (400 MHz, $CDCl_3$) δ: 8.23 (ovrlp, 2 H), 7.14 (s, 1 H), 4.25 (br s, 2 H). **^{13}C NMR (1°)** (100 MHz, $CDCl_3$) δ: 142.9, 140.2 (q, $^{4}J_{CF}$ = 1.2 Hz), 135.6 (q, $^{3}J_{CF}$ = 4.8 Hz), 127.0 (q, $^{2}J_{CF}$ = 32.3 Hz), 123.6 (q, $^{1}J_{CF}$ = 270.9 Hz), 117.4 (q, $^{3}J_{CF}$ = 3.6 Hz). **HRMS** (ESI) Calcd for $C_6H_5F_3N_2$ [M+H] (**1°**): 163.0478; Found: 163.0477; Calcd for $C_{12}H_7F_6N_3$ [M+H]$^{+}$: 308.0617; Found: 308.0635.



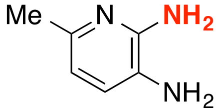
2-Amino-6-methoxypyridine (5c).[33] Following the general procedure A, the title compound was prepared using 2-chloro-6-methoxypyridine (143.6 mg, 119 μL, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:5) and then EtOAc/hexanes (1:3) as eluents to afford 2-amino-6-methoxypyridine (**5c**) (107.8 mg, 0.87 mmol, 87%) as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.32 (t, J = 8.0 Hz, 1 H), 6.08 (d, J = 8.0 Hz, 1 H), 6.04 (d, J = 7.6 Hz, 1 H), 4.44 (br s, 2 H), 3.83 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 163.7, 157.4, 140.3, 99.8, 98.3, 53.3. **IR** (neat cm^{-1}) 3473, 3371, 2949, 1575, 1452, 1416, 1340, 1253, 1150, 1120, 1028, 958, 780, 729. **Anal.** Calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; Found: C, 58.45; H, 6.76.



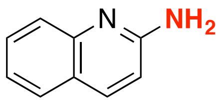
2-Amino-5-methylpyridine (5d).[34] Following the general procedure A, the title compound was prepared using 2-chloro-5-methylpyridine (127.6 mg, 109 μL, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with EtOAc/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford 2-amino-5-methylpyridine (**5d**) (81.1 mg, 0.75 mmol, 75%) as a pale-yellow solid. **m.p.:** 74-75 °C (lit: 76-77 °C).[34] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.88 (s, 1 H), 7.23 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1 H), 6.42 (d, *J* = 8.0 Hz, 1 H), 4.50 (br s, 2 H), 2.16 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.6, 147.5, 138.7, 122.7, 108.4, 17.4. **IR** (neat cm^{-1}) 3451, 3299, 3161, 2921, 1626, 1564, 1499, 1390, 1317, 1265, 1143, 1021, 824, 752, 652. **Anal.** Calcd. for $C_6H_8N_2$: C, 66.64; H, 7.46; Found: C, 66.88; H, 7.45.



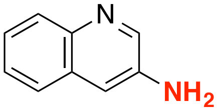
***tert*-Butyl 6-aminonicotinate (5e).**[35] Following the general procedure A, the title compound was prepared using *tert*-butyl 6-bromonicotinate (258.1 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:2) and then EtOAc/hexanes (2:1) as eluents to afford *tert*-butyl 6-aminonicotinate (**5e**) (113.8 mg, 0.59 mmol, 59%) as an off-white solid. **m.p.:** 101-102 °C (lit: 94-96 °C).[35] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.66 (d, *J* = 1.6 Hz, 1 H), 7.94 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1 H), 6.45 (d, *J* = 8.8 Hz, 1 H), 5.48 (br s, 2 H), 1.57 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 165.1, 161.2, 151.1, 138.7, 117.6, 107.3, 80.7, 28.3. **IR** (neat cm^{-1}) 3389, 3152, 1685, 1654, 1598, 1514, 1364, 1288, 1172, 1126, 1012, 834, 782. **Anal.** Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; Found: C, 61.44; H, 7.04.



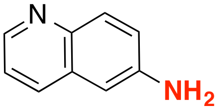
2,3-Diamino-6-methylpyridine (5f).[36] Following the general procedure A, the title compound was prepared using 2-chloro-3-amino-6-methylpyridine (142.6 mg, 1.0 mmol) and NaO^{t}Bu (211.4 mg, 2.2 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (10:1) as eluents to afford 2,3-diamino-6-methylpyridine (**5f**) (46.8 mg, 0.38 mmol, 38%) as a deep-brown solid. The yield of **5f** was determined to be 75% (NMR yield) based on 0.25 mmol heteroaryl halide using 1,3,5-trimethoxybenzene as internal standard. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.80 (d, *J* = 7.6 Hz, 1 H), 6.45 (d, *J* = 7.6 Hz, 1 H), 4.39 (br s, 2 H), 3.29 (br s, 2 H), 2.33 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.9, 147.0, 126.2, 123.7, 114.2, 23.1. **IR** (neat cm^{-1}) 3185, 2920, 1616, 1473, 1375, 1265, 1221, 1121, 1031, 802, 733. **HRMS** (ESI) Calcd for $C_6H_9N_3$ [M+H]: 124.0869; Found: 124.0868.



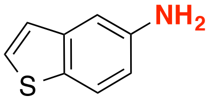
2-Aminoquinoline (5g).[37] Following the general procedure A, the title compound was prepared using 2-chloroquinoline (163.6 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EA/hexanes (20:1) as eluents to afford 2-aminoquinoline (**5g**) (83.6 mg, 0.58 mmol, 58%) as a pale-brown solid. **m.p.:** 126-127 °C (lit: 127-128 °C).[37] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.8 Hz, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 8.0 H, 1 H), 7.22 (t, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 8.8 Hz, 1 H), 5.30 (br s, 2 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 157.3, 147.6, 138.0, 129.7, 127.5, 125.7, 123.5, 122.5, 111.9. **IR** (neat cm^{-1}) 3422, 3301, 3122, 1647, 1563, 1509, 1483, 1429, 1393, 1354, 1123, 822, 751, 702, 621. **Anal.** Calcd. for $C_9H_8N_2$: C, 67.16; H, 4.51; Found: C, 67.04; H, 4.46.



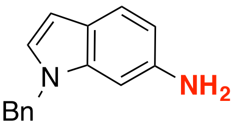
3-Aminoquinoline (5h).[38] Following the general procedure A, the title compound was prepared using 3-bromoquinoline (208.1 mg, 136 μL, 1.0 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc (100%) as an eluent to afford 3-aminoquinoline **(5h)** (137.9 mg, 0.95 mmol, 95%) as a brown solid. **m.p.:** 81 °C (lit: 80-83 °C).[39] **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 8.47 (d, *J* = 2.4 Hz, 1 H), 7.96 (d, *J* = 7.2 Hz, 1 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 7.42-7.36 (ovrlp, 2 H), 7.12 (d, *J* = 2.8 Hz, 1 H), 4.08 (br s, 2 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 143.1, 142.5, 140.0, 129.2, 128.9, 126.9, 125.8, 125.4, 114.7. **IR** (neat cm^{-1}) 3315, 3158, 1608, 1495, 1433, 1345, 1289, 1219, 1128, 978, 882, 838, 771, 743. **Anal.** Calcd. for $C_9H_8N_2$: C, 74.98; H, 5.59; Found: C, 74.70 H, 5.54.



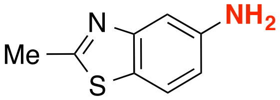
6-Aminoquinoline (5i).[40] Following the general procedure A, the title compound was prepared using 6-chloroquinoline (163.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc as an eluent to afford 6-aminoquinoline (**5i)** (130.7 mg, 0.91 mmol, 91%) as a brown solid. **m.p.:** 113-114 °C (lit: 115-116 °C).[41] **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 8.63 (d, *J* = 3.2 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.20 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1 H), 7.10 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 1 H), 6.81 (s, 1 H), 4.13 (br s, 2 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 146.5, 144.8, 143.2, 133.7, 130.2, 129.7, 121.6, 121.3, 107.2. **IR** (neat cm^{-1}) 3397, 3311, 3180, 1635, 1616, 1505, 1439, 1375, 1282, 1238, 1146, 1122, 959, 910, 824, 761. **Anal.** Calcd. for $C_9H_8N_2$: C, 74.98; H, 5.59; Found: C, 54.67; H, 5.84.



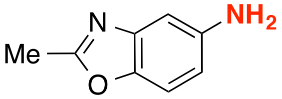
5-Aminobenzothiophene (5j).[42] Following the general procedure A, the title compound was prepared using 5-chlorobenzothiophene (168.6 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:4) and then EtOAc/hexanes (1:3) as eluents to afford 5-aminobenzothiophene (**5j**) (136.2 mg, 0.91 mmol, 91%) as a brown solid. **m.p.:** 71-72 °C (lit:71.2 °C**).**[43] **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 7.58 (d, *J* = 8.8 Hz, 1 H), 7.33 (d, *J* = 5.6 Hz, 1 H), 7.45 (d, *J* = 5.6 Hz, 1 H), 7.01 (d, *J* = 2.0 Hz, 1 H), 6.70 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1 H), 3.62 (br s, 2 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 143.6, 140.9, 130.3, 127.1, 123.1, 123.0, 114.9, 108.2. **IR** (neat cm^{-1}) 3427, 3347, 1594, 1502, 1428, 1268, 1246, 1163, 862, 839, 798, 764, 702. **Anal.** Calcd. for C_8H_7NS: C, 64.39; H, 4.73; Found: C, 64.73; H, 4.95.



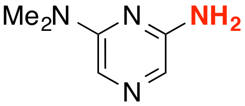
1-Benzyl-6-amino-1*H*-indole (5k). Following the general procedure A, the title compound was prepared using 1-benzyl-6-chloro-1*H*-indole (**S2**) (241.7 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:4) and then EtOAc/hexanes (1:2) as eluents to afford 1-benzyl-6-amino-1*H*-indole (**5k**) (203.4 mg, 0.91 mmol, 91%) as a brown solid. **m.p.:** 143-144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 8.4 Hz, 1 H), 7.27-7.16 (ovrlp, 3 H), 7.04 (d, J = 7.2 Hz, 2 H), 6.88 (d, J = 2.8 Hz, 1 H), 6.51 (d, J = 8.0 Hz, 1 H), 6.47 (s, 1 H), 6.40 (d, J = 2.8 Hz, 1 H), 5.13 (s, 2 H), 3.49 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.1, 137.8, 137.6, 128.8, 127.5, 126.7, 126.5, 122.0, 121.6, 110.6, 101.7, 95.3, 49.9. **IR** (neat cm^{-1}) 3436, 3351, 1624, 1493, 1469, 1454, 1432, 1337, 1325, 1278, 1228, 1180, 803, 734, 723. **Anal.** Calcd. for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; Found: C, 80.75; H, 6.42.



5-Amino-2-methylbenzothiazole (5l).[44] Following the general procedure A, the title compound was prepared using 5-chloro-2-methylbenzothiazole (183.7 mg, 1.0 mmol) at 60 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) and then EtOAc/hexanes (4:1) as eluents to afford 5-amino-2-methylbenzothiazole (**5l**) (155.5 mg, 0.95 mmol, 95%) as a pale-brown solid. **m.p.:** 100-101 °C (lit: 103.5-105 °C).[44] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.52 (d, J = 8.0 Hz, 1 H), 7.23 (s, 1 H), 6.72 (d, J = 7.2 Hz, 1 H), 3.85 (br s, 2 H), 2.76 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 167.8, 154.8, 145.4, 125.3, 121.6, 114.5, 107.4, 20.0. **IR** (neat cm^{-1}) 3383, 3308, 3196, 1635, 1556, 1522, 1469, 1436, 1316, 1173, 1152, 947, 857, 797, 693, 646. **Anal.** Calcd. for $C_8H_8N_2S$: C, 58.51; H, 4.91; Found: C, 58.44; H, 5.03.



5-Amino-2-methylbenzoxazole (5m).[45] Following the general procedure A, the title compound was prepared using 5-chloro-2-methylbenzoxazole (167.6 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (4:1) and then EtOAc/MeOH (10:1) as eluents to afford 5-amino-2-methylbenzoxazole (**5m**) (103.8 mg, 0.70 mmol, 70%) as a pale-brown solid. The 1° : 2° ratio was determined to be 10 : 1 in the crude product based on 0.25 mmol hereroaryl halide. **m.p.:** 71-73 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.21 (d, J = 8.8 Hz, 1 H), 6.92 (d, J = 2.0 Hz, 1 H), 6.61 (dd, J = 8.4 Hz, J = 2.0 Hz, 1 H), 3.77 (s, 2 H), 2.55 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 164.3, 144.8, 143.6, 142.4, 112.8, 110.2, 104.7, 14.5. **IR** (neat cm^{-1}) 3420, 3348, 1622, 1568, 1486, 1450, 1381, 1272, 1176, 923, 841, 804, 688, 660, 616. **HRMS** (ESI) Calcd for $C_8H_8N_2O$ [M+H]: 149.0709; Found: 149.0709.

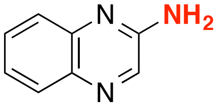


2-Amino-6-(dimethylamino)pyrazine (5n).

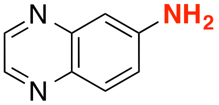
(i) 50 °C. Following the general procedure A, the title compound was prepared using 2-chloro-6-(dimethylamino)pyrazine (157.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford an inseparable deep-brown mixture of 2-amino-6-(dimethylamino)pyrazine (**5n**) (91.9 mg, 0.62 mmol, 62%) and bis(6-(dimethylamino)pyrazin-2-

yl)amine (**5n'**) (4%). The 1° : 2° ratio was determined to be 16:1 of the isolated product mixture. **^{1}H NMR of 1° product** (400 MHz, CDCl$_3$) δ: 7.37 (s, 1 H), 7.24 (s, 1 H), 4.35 (br s, 2 H), 3.03 (s, 6 H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ: 154.0, 152.6, 118.8, 118.0, 37.5. **IR** (neat cm^{-1}) 3423, 3276, 3114, 1629, 1575, 1525, 1428, 1389, 1307, 1230, 1204, 1160, 1106, 910, 802, 668. **HRMS** (ESI) Calcd for $C_6H_{10}N_4$ [M+H] (**1°**) 139.9078; Found: 139.0972; Calcd for $C_{12}H_{17}N_7$ [M+H] (**2°**): 260.1618; Found: 260.1632.

(ii) rt. Following the general procedure A, the title compound was prepared using 2-chloro-6-(dimethylamino)pyrazine (157.6 mg, 1.0 mmol), Pd precatalyst **3a** (27.6 mg, 0.030 mmol), and **L6** (16.5 mg, 0.030 mmol) at room temperature. After work up the crude product was purified by flash chromatography with alumina using EtOAc/hexanes (1:4) and then EtOAc as eluents to afford an inseparable deep-brown mixture of 2-amino-6-(dimethylamino)pyrazine (**5n**) (114.7 mg, 0.62 mmol, 83%) and bis(6-(dimethylamino)pyrazin-2-yl)amine (**5n'**) (3%). The 1° : 2° ratio was determined to be 29:1 of the isolated product mixture based on 0.25 mmol heteroaryl halide. Spectral and analytical data were identical to those reported for the same compound above.



2-Aminoquinoxaline (5o).[46] Following the general procedure A, the title compound was prepared using 2-chloroquinoxaline (164.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc/hexanes (1:4) and then EtOAc/hexanes (5:1) as eluents to afford 2-aminoquinoxaline (**5o**) (101.8 mg, 0.70 mmol, 70%) as a yellow solid. **m.p.:** 155-157 °C (lit: 155-157 °C).[47] **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 8.31 (d, J = 1.6 Hz, 1 H), 7.76 (d, J = 8.4 Hz, 1 H), 7.55-7.49 (ovrlp, 2 H), 7.34-7.28 (m, 1 H), 6.98 (br s, 2 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 153.6, 141.9, 139.2, 136.4, 129.6, 128.5, 125.4, 123.4. **IR** (neat cm^{-1}) 3318, 3116, 1743, 1658, 1586, 1568, 1481, 1425, 1353, 1238, 1125, 1025, 976, 915, 752. **HRMS** (ESI) Calcd for $C_8H_7N_3$ [M+H]: 146.0713; Found: 146.0710.

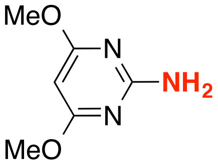


6-Aminoquinoxaline (5p).[48]

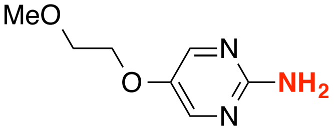
(i) 50 °C. Following the general procedure A, the title compound was prepared using 6-bromoquinoxaline (209.0 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford 6-aminoquinoxaline (**5p**) (127.4 mg, 0.88 mmol, 88%) as a deep brown solid. **m.p.:** 155-156 °C (lit: 157 °C).[48] **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 8.60 (d, J = 1.6 Hz, 1 H), 8.44 (d, J = 2.0 Hz, 1 H), 7.73 (d, J = 9.2 Hz, 1 H), 7.25 (dd, J = 9.2 Hz, J = 2.4 Hz, 1 H), 6.93 (d, J = 2.4 Hz, 1 H), 6.08 (br s, 2 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 150.5, 145.0, 144.9, 139.7, 136.5, 129.7, 122.4, 105.0. **IR** (neat cm^{-1}) 3393, 3312, 3182, 1645, 1611, 1501, 1434, 1370, 1307, 1225, 1134, 1031, 959, 857, 816. **HRMS** (ESI) Calcd for $C_8H_7N_3$ [M+H]: 146.0713. Found: 146.0713.

(ii) rt. Following the general procedure A, the title compound was prepared using 6-bromoquinoxaline (209.0 mg, 1.0 mmol), Pd precatalyst **3a** (27.6 mg, 0.030 mmol), and **L6** (16.5 mg, 0.030 mmol) at room temperature. After work up the crude product was purified by flash chromatography with silica gel using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford 6-aminoquinoxaline (**5p**) (126.8 mg, 0.87 mmol, 87%) as a deep brown solid. Spectral and analytical data were identical to those reported for the same compound above. **^{1}H NMR** (400 MHz, CDCl$_3$) δ: 8.66 (d, J = 2.0 Hz, 1 H), 8.55 (d, J = 2.0 Hz, 1

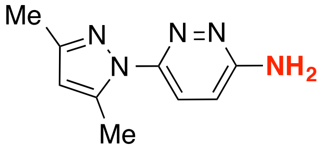
H), 7.88 (d, $J = 9.2$ Hz, 1 H), 7.19 (dd, $J = 9.2$ Hz, $J = 2.4$ Hz, 1 H), 7.15 (d, $J = 2.4$ Hz, 1 H), 4.40 (br s, 2 H).



2-Amino-4,6-dimethoxypyrimidine (5q).[49] Following the general procedure A, the title compound was prepared using 2-chloro-4,6-dimethoxypyrimidine (174.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) as an eluent to afford 2-amino-4,6-dimethoxypyrimidine (**5q**) (124.1 mg, 0.80 mmol, 80%) as a white solid. **m.p.:** 97-98 °C (lit: 95 °C).[49] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.46 (s, 1 H), 5.40 (s, 2 H), 3.83 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 172.4, 162.5, 79.4, 53.7. **IR** (neat cm^{-1}) 3407, 3308, 3181, 1633, 1569, 1444, 1409, 1360, 1210, 1147, 1100, 1043, 1008, 926, 791, 769, 681. **HRMS** (ESI) Calcd for $C_6H_9N_3O_2$ [M+H]: 156.0768; Found: 156.0759.

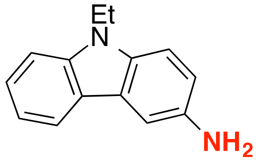


2-amino-5-(2-methoxyethoxy)pyrimidine (5r). Following the general procedure **A**, the title compound was prepared using 2-chloro-5-(2-methoxyethoxy)pyrimidine (**S5**) (377.2 mg, 2.0 mmol), NH_3 solution (0.5 M, 6.0 mmol, 12.0 mL), NaO^{t}Bu (269.1 mg, 2.8 mmol), Pd precatalyst **3a** (36.7 mg, 0.040 mmol), **L6** (22.0 mg, 0.040 mmol), and 1,4-dioxane (1.0 mL) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (15:1) as an eluent to afford 2-amino-5-(2-methoxyethoxy)pyrimidine (**5q**) (214.6 mg, 0.63 mmol, 63%) as a white solid. **m.p.:** 79-81 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.08 (s, 2 H), 5.55 (br s, 2 H), 4.09 (t, $J = 4.8$ Hz, 2 H), 3.71 (t, $J = 4.8$ Hz, 2 H), 3.43 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.8, 146.3, 146.2, 70.8, 69.2, 58.9. **IR** (neat cm^{-1}) 3403, 3315, 3196, 2883, 1630, 1553, 1466, 1266, 1189, 1123, 1065, 1035, 908, 863, 783, 650. **Anal.** Calcd. for $C_7H_{11}N_3O_2$: C, 49.70; H, 6.55; Found: C, 49.78; H, 6.58.

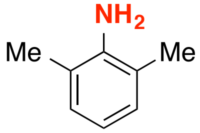


3-Amino-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine (5s). Following the general procedure A, the title compound was prepared using 3-chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine (208.7 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford 3-amino-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine (**5s**) (67.4 mg, 0.36 mmol, 36%) as a brown solid. The ^{1}H NMR of **5s** was determined to be 56% based on 0.25 mmol reaction using 1,3,5-trimethoxybenzene as internal standard. **m.p.:** 141-142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.78 (d, $J = 9.2$ Hz, 1 H), 6.89 (d, $J = 9.2$ Hz, 1 H), 6.00 (s, 1 H), 5.20 (br s, 2 H), 2.59 (s, 3 H), 2.28 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.3, 150.9, 150.0, 141.4, 123.7, 117.3, 108.7, 14.0, 13.6. **IR** (neat cm$^-$

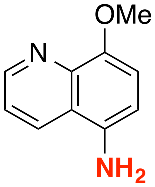
^{1}) 3306, 3139, 1624, 1552, 1476, 1436, 1338, 1219, 1034, 1016, 971, 836, 793. **Anal.** Calcd. for $C_9H_{11}N_5$: C, 57.13; H, 5.86; Found: C, 57.02; H, 5.73.



3-Amino-9-ethyl-9*H*-carbazole (5t).[50] Following the general procedure A, the title compound was prepared using 3-bromo-9-ethyl-9*H*-carbazole (274.2 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:2) and then EtOAc/hexanes (2:1) as eluents to afford 3-amino-9-ethyl-9*H*-carbazole (**5t**) (183.6 mg, 0.87 mmol, 87%) as a brown solid. **m.p.:** 109-112 °C (lit: 113-114 °C).[50] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 1 H), 7.42-7.38 (ovrlp, 2 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 7.13 (t, *J* = 7.6 Hz, 1 H), 6.87 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 3.55 (br s, 2 H), 1.35 (t *J* = 7.2 Hz, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 140.3, 139.0, 134.4, 125.4, 123.6, 122.4, 120.4, 118.0, 115.5, 109.0, 108.3, 106.3, 37.4, 13.8. **IR** (neat cm^{-1}) 3412, 3332, 2973, 1606, 1492, 1468, 1327, 1227, 1147, 802, 747. **HRMS** (ESI) Calcd for $C_{14}H_{14}N_2$ [M+H]: 211.1230. Found: 211.1221.

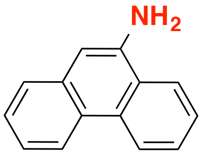


2,6-Dimethylaniline (6a).[51] Following procedure B, the title compound was prepared using 2-chloro-1,3-xylene (140.6 mg, 133 μL, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:15) as an eluent to afford 2,6-dimethylaniline (**6a**) (86.1 mg, 0.71 mmol, 71%) as a brown oil. The 1° : 2° ratio was determined to be 29:1 of the isolated product mixture based on 0.25 mmol aryl halide; a trace of reduced product xylene was also detected by GC/MS analysis. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 6.93 (d, *J* = 7.6 Hz, 2 H), 6.63 (t, *J* = 7.6 Hz, 1 H), 3.53 (br s, 2 H), 2.16 (s, 6 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 142.8, 128.3, 121.8, 118.1, 17.7. **IR** (neat cm^{-1}) 3386, 2966, 2919, 2853, 1617, 1474, 1272, 1089, 756, 733. **HRMS** (ESI) Calcd for $C_8H_{11}N$ [M+H]: 122.0964; Found: 122.0964.

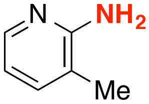


5-Amino-8-methoxyquinoline (6b).[52] Following the general procedure B, the title compound was prepared using 5-chloro-8-methoxyquinoline (**S9**) (193.6 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (15:1) as eluents to afford 5-amino-8-methoxyquinoline (**6b**) (160.6 mg, 0.92 mmol, 92%) as a deep-brown solid. **m.p.:** 152-153 °C (lit: 156-158 °C).[52] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.93-8.91 (m, 1 H), 8.17 (d, *J* = 8.4 Hz, 1 H), 7.40-7.36 (m, 1 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 4.01 (s, 3 H), 3.80 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 148.8, 148.6, 140.2, 134.9, 129.9, 120.3, 120.2, 110.0, 108.1, 55.8. **IR** (neat cm^{-1})

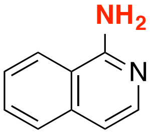
3318, 3215, 1635, 1475, 1461, 1419, 1365, 1276, 1250, 1098, 1016, 819, 785, 703, 643. **HRMS** (ESI) Calcd for $C_{10}H_{10}N_2O$ [M+H]: 175.0866; Found: 175.0858.



9-Aminophenanthrene (6c).[53] Following procedure B, the title compound was prepared using 9-bromophenanthrene (257.1 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:6) and then EtOAc/hexanes (1:4) as an eluent to afford 9-aminophenanthrene (**6c**) (159.1 mg, 0.82 mmol, 82%) as a brown solid. A reduced product, phenanthrene, also formed in 8% NMR yield based on 0.25 mmol aryl halide using 1,3,5-trimethoxybenzene as internal standard. **m.p.:** 135-136 °C (lit: 137.5-139 °C).[53] **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ: 8.74 (d, *J* = 7.6 Hz, 1 H), 8.57 (d, *J* = 8.0 Hz, 1 H), 8.23 (d, *J* = 7.6 Hz, 1 H), 7.67-7.62 (ovrlp, 2 H), 7.59 (d, *J* = 8.0 Hz, 1 H), 7.43 (t, *J* = 7.6 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 6.91 (s, 1 H), 5.80 (br s, 2 H). **^{13}C NMR** (100 MHz, DMSO-*d*$_6$) δ: 142.5, 133.8, 130.6, 126.8, 126.5, 125.9, 125.4, 125.0, 124.3, 123.1, 122.7, 122.5, 121.9, 103.8. **IR** (neat cm^{-1}) 3391, 3322, 1497, 1631, 1607, 1434, 1323, 1236, 1206, 869, 845, 719, 644. **HRMS** (ESI) Calcd for $C_{14}H_{11}N$ [M+H]: 194.0964; Found: 194.0950.



2-Amino-3-methylpyridine (6d).[54] Following the general procedure B, the title compound was prepared using 2-chloro-3-methylpyridine (127.6 mg, 109 μL, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/Et_3N (50:1)) using EtOAc and then EtOAc/MeOH (20:1) as eluents to afford an inseparable pale brown oily mixture of 2-amino-3-methylpyridine (**6d**) (91.9 mg, 0.85 mmol, 85%) and bis(3-methylpyridin-2-yl)amine (**6d'**) (8%). The 1° : 2° ratio was determined to be 11 : 1 in the isolated product mixture. **^{1}H NMR (1°)** (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 4.0 Hz, 1 H), 7.24 (d, *J* = 7.2 Hz, 1 H), 6.59 (dd, *J* = 7.2 Hz, *J* = 4.8 Hz, 1 H), 4.57 (br s, 2 H), 2.10 (s, 3 H). **^{13}C NMR (1°)** (100 MHz, $CDCl_3$) δ: 157.3, 145.6, 137.7, 116.6, 114.3, 17.1. **IR** (neat cm^{-1}) 3324, 3190, 1613, 1594, 1579, 1470, 1451, 1382, 1290, 1196, 1079, 1036, 994, 764. **HRMS** (ESI) Calcd for $C_6H_8N_2$ [M+H] (**1°**): 109.0760. Found: 109.0760; Calcd for $C_{12}H_{13}N_3$ (**2°**): [M+H]: 200.1182. Found: 200.1168.

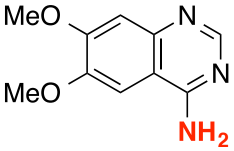


1-Aminoisoquinoline (6e).[55]

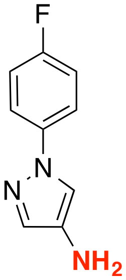
(i) 50 °C. Following the general procedure B, the title compound was prepared using 1-chloroisoquinoline (163.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc/hexanes (2:1) followed by EtOAc/hexanes (4:1) and EtOAc/hexanes (10:1) as eluents to afford 1-aminoisoquinoline (**6e**) (109.4 mg, 0.76 mmol, 76%) as a yellow solid. **m.p.:** 119-120 °C.(lit: 122-123 °C).[55] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 5.6 Hz, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* =

8.0 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 7.02 (d, *J* = 6.0 Hz, 1 H), 5.49 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 156.5, 141.2, 137.4, 130.2, 127.1, 126.1, 122.7, 117.9, 112.4. **IR** (neat cm^{-1}) 3486, 3305, 3054, 1639, 1560, 1503, 1434, 1342, 1287, 1259, 1145, 1006, 873, 800, 751, 676. **HRMS** (ESI) Calcd for $C_9H_8N_2$ [M+H]: 145.0760; Found: 145.0758.

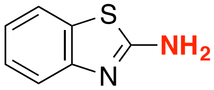
(ii) rt. Following the general procedure B, the title compound was prepared using 1-chloroisoquinoline (163.6 mg, 1.0 mmol), Pd precatalyst **3b** (45.3 mg, 0.050 mmol), and **L7** (26.8 mg, 0.050 mmol) at room temperature. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc/hexanes (2:1) followed by EtOAc/hexanes (4:1) and EtOAc/hexanes (10:1) as eluents to afford 1-aminoisoquinoline (**9e**) (116.0 mg, 0.81 mmol, 81%) as a yellow solid. Spectral and analytical data were identical to those reported for the same compound above.



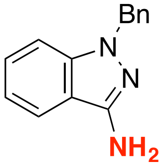
4-Amino-6,7-dimethoxyquinazoline (**6f**).[56] Following the general procedure B, the title compound was prepared using 4-chloro-6,7-dimethoxyquinazoline (224.6 mg, 1.0 mmol) at 50 °C. After work up the crude product was purified by flash chromatography with alumina using EtOAc followed by EtOAc/MeOH (20:1) and EtOAc/MeOH (15:1) as eluents to afford 4-amino-6,7-dimethoxyquinazoline (**6f**) (176.6 mg, 0.86 mmol, 86%) as a yellow solid. The diarylamine side-product was detected by LC/MS analysis and the 1° : 2° ratio was determined to be 9 : 1 in the crude product based on 0.25 mmol aryl halide. **m.p.:** 201-202 °C (lit: 202 °C).[56] **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 8.27 (s, 1 H), 7.57 (s, 1 H), 7.42 (br s, 2 H), 7.07 (s, 1 H), 3.89 (s, 3 H), 3.86 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 160.5, 154.0, 153.9, 148.2, 146.7, 108.0, 106.9, 102.7, 56.0, 55.7. **IR** (neat cm^{-1}) 3586, 3302, 3089, 2924, 1665, 1584, 1487, 1435, 1339, 1248, 1218, 1117, 1031, 990, 833, 788. **HRMS** (ESI) Calcd for $C_{10}H_{11}N_3O_2$ [M+H]: 206.0924; Found: 206.0914.



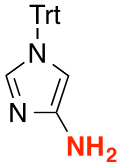
4-Amino-1-(4-fluorophenyl)-1*H*-pyrazole (7a). An oven-dried 25 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with 4-bromo-1-(4-fluorophenyl)pyrazole (241.1 mg, 1.0 mmol, 1.0 equiv) and sodium *tert*-butoxide (134.5 mg, 1.4 mmol, 1.4 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 6.0 mL, 3.0 mmol, 3.0 equiv) was then added into tube **A** via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd_2dba_3 (9.2 mg, 0.01 mmol, 0.01 equiv) and ligand **L4** (25.6 mg, 0.04 mmol, 0.04 equiv). Tube **B** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (4.0 mL) was then added into tube **B** via syringe. The reaction mixture in tube **B** was stirred at 100 °C in an oil bath for 3 min, after which time the color of the reaction mixture changed from dark purple to deep brown, indicating the formation of Pd-**L4** catalyst. After cooling to room temperature, the deep brown catalyst solution from tube **B** was transferred into tube **A** via syringe. The reaction mixture in tube **A** was then stirred in an oil bath at 120 °C for 20 h. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator. The crude product residue was then purified by flash column chromatography with silica gel using EtOAc and then EtOAc/MeOH (15:1) as an eluent to afford 4-amino-1-(4-fluorophenyl)-1*H*-pyrazole (**7a**) (153.3 mg, 0.86 mmol, 86%) as a brown solid (78% ^{1}H NMR yield based on 0.25 mmol heteroaryl halide using 1,3,5-trimethoxybenzene as internal standard). Note: the conversion was incomplete when catalyst system **3c/L4** was used based on 0.25 mmol heteroaryl halide. **m.p.:** 86-87 °C. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ: 7.54 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 4.8 Hz, 2 H), 7.43 (s, 1 H), 7.37 (s, 1 H), 7.09 (dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HF}$ = 8.8 Hz, 2 H), 3.06 (br s, 2 H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ: 160.5 (d, $^1J_{CF}$ = 243.1 Hz), 136.7 (d, $^4J_{CF}$ = 2.6 Hz), 133.4, 131.3, 119.8 (d, $^3J_{CF}$ = 8.1 Hz), 116.0 (d, $^2J_{CF}$ = 22.7 Hz), 114.6. **IR** (neat cm^{-1}) 3399, 3286, 3197, 3130, 1588, 1514, 1398, 1367, 1225, 1091, 1011, 949, 832, 809, 647. **Anal.** Calcd. for $C_9H_8FN_3$: C, 61.01; H, 4.55; Found: C, 61.26; H, 4.63.



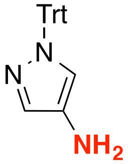
2-Aminobenzothiazole (7b).[57] Following the general procedure C, the title compound was prepared using 2-chlorobenzothiazole (169.6 mg, 130 μL, 1.0 mmol), precatalyst **3c** (50.5 mg, 0.050 mmol), **L4** (32.0 mg, 0.050 mmol), and 1,4-dioxane (1 mL) at room temperature. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:2) and then EtOAc/hexanes (2:1) as eluents to afford 2-aminobenzothiazole (**7b**) (144.5 mg, 0.96 mmol, 96%) as a pale-brown solid. **m.p.:** 128-129 °C (lit: 125-127 °C).[57] ^{1}**H NMR** (400 MHz, DMSO-d_6) δ: 7.64 (d, J = 8.0 Hz, 1 H), 7.44 (br s, 2 H), 7.33 (d, J = 8.0 Hz, 1 H), 7.20 (td, J = 8.0 Hz, J = 0.8 Hz, 1 H), 6.99 (td, J = 8.0 Hz, J = 0.8 Hz, 1 H). ^{13}**C NMR** (100 MHz, DMSO-d_6) δ: 166.4, 152.8, 130.9, 125.4, 120.85, 120.78, 117.7. **IR** (neat cm^{-1}) 3388, 3055, 1639, 1524, 1443, 1307, 1283, 1103, 888, 739, 719. **HRMS** (ESI) Calcd for $C_7H_8N_2S$ [M+H]: 151.0324; Found: 151.0318.



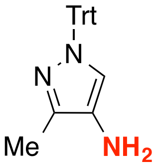
3-Amino-1-benzyl-1*H*-indazole (7c).[58] Following the general procedure C, the title compound was prepared using 1-benzyl-3-chloro-1*H*-indazole (**S6**) (242.7 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) and then EtOAc/hexanes (2:1) as eluents to afford 3-amino-1-benzyl-1*H*-indazole (**7c**) (175.8 mg, 0.79 mmol, 79%) as a brown solid. A trace of reduced product, 1-benzyl-1*H*-indazole, formed based on 0.25 mmol heteroaryl halide as detected by GC/MS. **m.p.:** 116-117 °C (lit: 111-113 °C).[58] ^{1}**H NMR** (400 MHz, $CDCl_3$) δ: 7.52 (dt, J = 8.4 Hz, J = 0.8 Hz, 1 H), 7.31-7.20 (ovrlp, 4 H), 7.19-7.15 (ovrlp, 3 H), 7.00 (ddd, J = 8.0 Hz, J = 6.8 Hz, J = 0.8 Hz, 1 H), 5.34 (s, 2 H), 4.11 (br s, 2 H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ: 147.5, 141.4, 137.6, 128.7, 127.6, 127.14, 127.13, 119.7, 118.8, 115.1, 109.0, 52.2. **IR** (neat cm^{-1}) 3432, 3301, 3196, 1623, 1541, 1493, 1438, 1353, 1307, 1264, 1082, 1027, 950, 815, 762, 744, 699. **HRMS** (ESI) Calcd for $C_{14}H_{13}N_3$ [M+H]: 224.1182; Found: 224.1161.



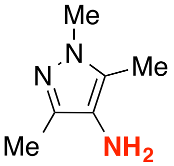
4-Amino-1-trityl-1*H*-imidazole (7d). Following the general procedure C, the title compound was prepared using 4-bromo-1-trityl-1*H*-imidazole (**S3**) (389.3 mg, 1.0 mmol) at 80 °C. After work up the crude product was purified by flash chromatography with silica gel (initially eluted with hexanes/triethylamine (50:1)) using EtOAc and then EtOAc/MeOH (12:1) as eluents to afford 4-amino-1-trityl-1*H*-imidazole (**7e**) (294.3 mg, 0.90 mmol, 90%) as a deep-brown solid. **m.p.:** 196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.33-7.30 (ovrlp, 9 H), 7.19-7.14 (m, 6 H), 7.09 (d, *J* = 1.6 Hz, 1 H), 6.08 (d, *J* = 1.6 Hz, 1 H), 3.29 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 144.7, 142.6, 135.2, 129.9, 128.04, 128.00, 103.8, 75.2. **IR** (neat cm^{-1}) 3412, 3297, 3052, 1569, 1489, 1442, 1378, 1241, 1140, 1084, 1036, 990, 907, 870, 751, 699, 638, 654. **HRMS** (ESI) Calcd for $C_{22}H_{19}N_3$ [M+H]: 326.1652; Found: 326.1659.



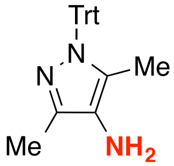
4-Amino-1-trityl-1*H*-pyrazole (7e). Following the general procedure C, the title compound was prepared using 4-bromo-1-trityl-1*H*-pyrazole (**S4**) (389.3 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) followed by EtOAc/hexanes (4:1) as eluents to afford 4-amino-1-trityl-1*H*-pyrazole (**7e**) (279.8 mg, 0.79 mmol, 79%) as an off-white solid. A small amount of reduced product, 1-benzyl-1*H*-indazole (9% NMR yield), formed based on 0.25 mmol heteroaryl halide using 1,3,5-trimethoxybenzene as internal standard. **m.p.:** 206-207 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 0.8 Hz, 1 H), 7.30-7.27 (ovrlp, 9 H), 7.18-7.13 (m, 6 H), 7.94 (d, *J* = 0.8 Hz, 1 H), 2.84 (br s, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.5, 132.1, 130.3, 127.8, 127.73, 127.67, 121.7, 78.4. **IR** (neat cm^{-1}) 3408, 3338, 3056, 1582, 1492, 1443, 1347, 1181, 990, 903, 874, 815, 748, 698, 638. **HRMS** (ESI) Calcd for $C_{22}H_{19}N_3$ [M+H]: 326.1652; Found: 326.1647.



4-Amino-3-methyl-1-trityl-1*H*-pyrazole (7f). Following the general procedure C, the title compound was prepared using 4-bromo-3-methyl-1-trityl-1*H*-pyrazole (**S7**) (403.3 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) and then EtOAc/hexanes (4:1) as eluents to afford 4-amino-3-methyl-1-trityl-1*H*-pyrazole (**7f**) (170.7 mg, 0.50 mmol, 50%) as a brown solid. **m.p.:** 191-192 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28-7.24 (ovrlp, 9 H), 7.18-7.14 (m, 6 H), 6.83 (s, 1 H), 2.67 (br s, 2 H), 2.17 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.8, 140.1, 130.2, 127.7, 127.5, 125.3, 122.2, 77.8, 11.1. **IR** (neat cm^{-1}) 3408, 3337, 3061, 1584, 1491, 1443, 1352, 1218, 1182, 1082, 1035, 998, 902, 874, 755, 698, 733, 641. **HRMS** (ESI) Calcd for $C_{23}H_{21}N_3$ [M+H]: 340.1808; Found: 340.1814.



4-Amino-1,3,5-trimethyl-1*H*-pyrazole (7g).[59] Following the general procedure B, the title compound was prepared using 4-bromo-1,3,5-trimethyl-1*H*-pyrazole (189.1 mg, 1.0 mmol) at 100 °C. After work up the crude product was purified by flash chromatography with alumina using EtOAc/hexanes (1:1) followed by EtOAc/hexanes (3:2) and EtOAc/hexanes (4:1) as eluents to afford 4-amino-1,3,5-trimethyl-1*H*-pyrazole (**7g**) (50.4 mg, 0.40 mmol, 40%) as a brown solid. The yield of **7g** was determined to be 78% (NMR yield) and a small amount of 1,3,5-trimethyl-1*H*-pyrazole (9% NMR yield) also formed based on 0.25 mmol heteroaryl halide using 1,3,5-trimethoxybenzene as internal standard. **m.p.:** 97-99 °C (lit: 98 °C).[59] **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 3.66 (s, 3 H), 2.52 (br s, 2 H), 2.15 (s, 3 H), 2.13 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.6, 128.0, 122.7, 36.1, 10.8, 8.8. **IR** (neat cm^{-1}) 3343, 3204, 2922, 1588, 1475, 1444, 1360, 1314, 1232, 988, 861, 803, 680, 613. **HRMS** (ESI) Calcd for $C_6H_{11}N_3$ [M+H]: 126.1026; Found: 126.1026.



4-Amino-3,5-dimethyl-1-trityl-1*H*-pyrazole (7h). Following the general procedure B, the title compound was prepared using 4-bromo-3,5-dimethyl-1-trityl-1*H*-pyrazole (**S8**) (417.3 mg, 1.0 mmol) at 110 °C. After work up the crude product was purified by flash chromatography with silica gel using EtOAc/hexanes (1:1) and then EtOAc as eluents to afford 4-amino-3,5-dimethyl-1-trityl-1*H*-pyrazole (**7h**) (291.2 mg, 0.82 mmol, 82%) as an off-white solid. A small amount of reduced product, 3,5-dimethyl-1-trityl-1*H*-pyrazole (8% NMR yield), also formed based on 0.25 mmol heteroaryl halide using 1,3,5-trimethoxybenzene as internal standard. **m.p.:** 211-212 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ: 7.31-7.22 (ovrlp, 9 H), 7.04-7.01 (m, 6 H), 3.45 (br s, 2 H), 1.99 (s, 3 H), 1.30 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ: 143.4, 135.3, 129.8, 127.4, 127.3, 126.9, 126.1, 76.8, 11.7, 11.3. **IR** (neat cm^{-1}) 3408, 3336, 2921, 1596, 1490, 1444, 1336, 1267, 1211, 1035, 1000, 895, 759, 744, 708, 697, 667, 642. **HRMS** (ESI) Calcd for $C_{24}H_{23}N_3$ [M+H]: 354.1965; Found: 354.1970.

Control Experiments for Palladium-Catalyzed Arylation of Ammonia (Scheme S2). An oven-dried 15 mL re-sealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with ligand (**L6**, **L7**, or **L4**; 0.005 mmol, 0.02 equiv), sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (0.25 mmol, 1.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). Ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv), 1,4-dioxane (1.0 mL), and (hetero)aryl halide (if liquid) (0.25 mmol, 1.0 equiv) were then added into the tube via syringe. The reaction mixture was stirred at an elevated temperature in an oil bath or at room temperature for 24 h. After cooling to room temperature, ethyl acetate (~4 mL) was added into the reaction mixture, and a portion of the reaction mixture was analyzed for the existence of the arylamine product by (i) GC/MS analysis, (ii) TLC analysis by comparing with the authentic samples, or (iii) ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.33 equiv) as internal standard.

Additional Results for the Selective Palladium-Catalyzed Arylation of Ammonia (Scheme S3). An oven-dried 15 mL re-sealable screw-cap test tube (**A**) equipped with a Teflon-coated magnetic stir bar was charged with ligand (**L6** or **L7**; 0.005 mmol, 0.02 equiv), sodium *tert*-butoxide (33.6 mg, 0.35 mmol, 1.4 equiv), and (hetero)aryl halide (if solid) (0.25 mmol, 1.0 equiv). Tube **A** was evacuated and backfilled with argon (this sequence was repeated a total of three times), and ammonia solution (0.5 M in 1,4-dioxane, 1.5 mL, 3.0 equiv) and (hetero)aryl halide (if liquid) (0.25 mmol, 1.0 equiv) were then added into the tube via syringe. Simultaneously, an oven-dried 10 mL re-sealable screw-cap test tube (**B**) equipped with a Teflon-coated magnetic stir bar was charged with Pd precatalyst (**3a** or **3b**; 0.005 mmol, 0.02 equiv). Tube **B** was then evacuated and backfilled with argon (this sequence was repeated a total of three times), and 1,4-dioxane (1.0 mL) was added into the tube via syringe. The reaction mixture in tube **B** was stirred at room temperature for ~1 min to form a homogeneous solution. The precatalyst solution from tube **B** was transferred into tube **A** via syringe. The reaction mixture in tube **A** was stirred at the required temperature (50 °C, 60 °C, 80 °C, or 100 °C) in an oil bath for 20 or 24 h. After cooling to room temperature, ethyl acetate (~4 mL) and 1,3,5-trimethoxybenzene (14.0 mg, 0.083 mmol, 0.33 equiv) were added into the reaction mixture. A portion of reaction mixture was concentrated *in vacuo* with the aid of a rotary evaporator to give crude product. The yield of arylamine product was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

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(9) Pd_2dba_3 and ligand were allowed to premix in 1,4-dioxane at 100 °C for 3 min to form a ligated palladium catalyst prior to the reaction in order to enhance the catalytic activity of Pd. See: Ueda, S.; Su, M. Buchwald, S. L. *J. Am. Chem. Soc.*, **2012**, *134*, 700–706.
(10) The transfer was carried out via syringe. However, the procedure should be carried as written as it is much safer!

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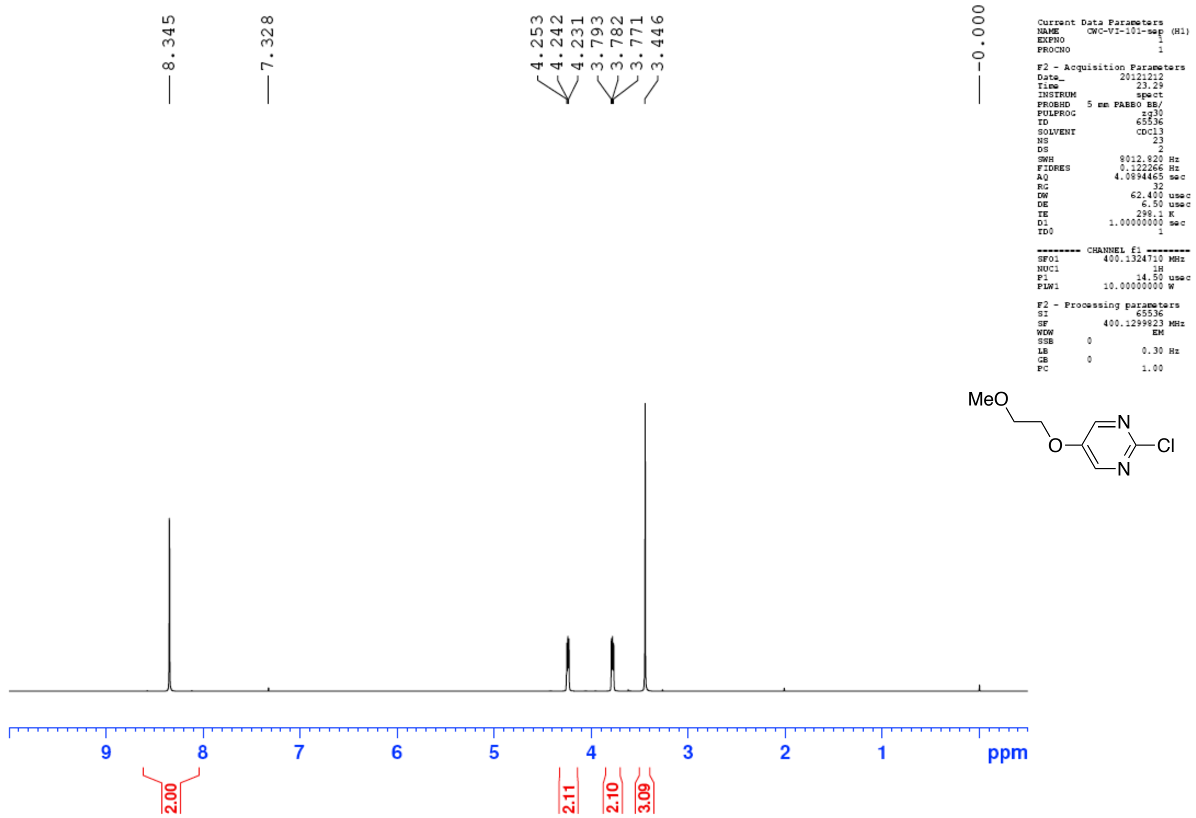
List of Spectra of Compounds

^{1}H and ^{13}C NMR of 2-chloro-5-(2-methoxyethoxy)pyrimidine (**S5**)



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FIDRES           0.122266 Hz
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DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

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PLW1          10.00000000 W

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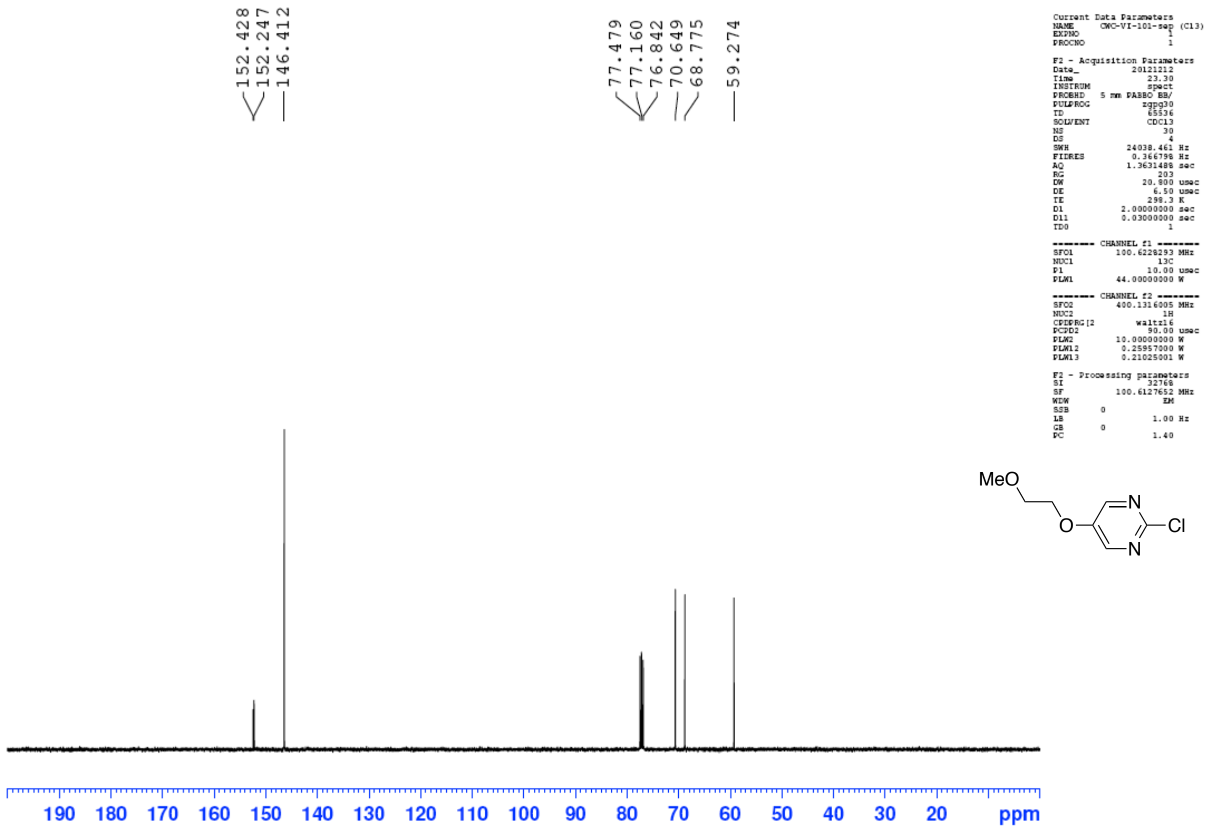

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FIDRES           0.366798 Hz
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P1                  10.00 usec
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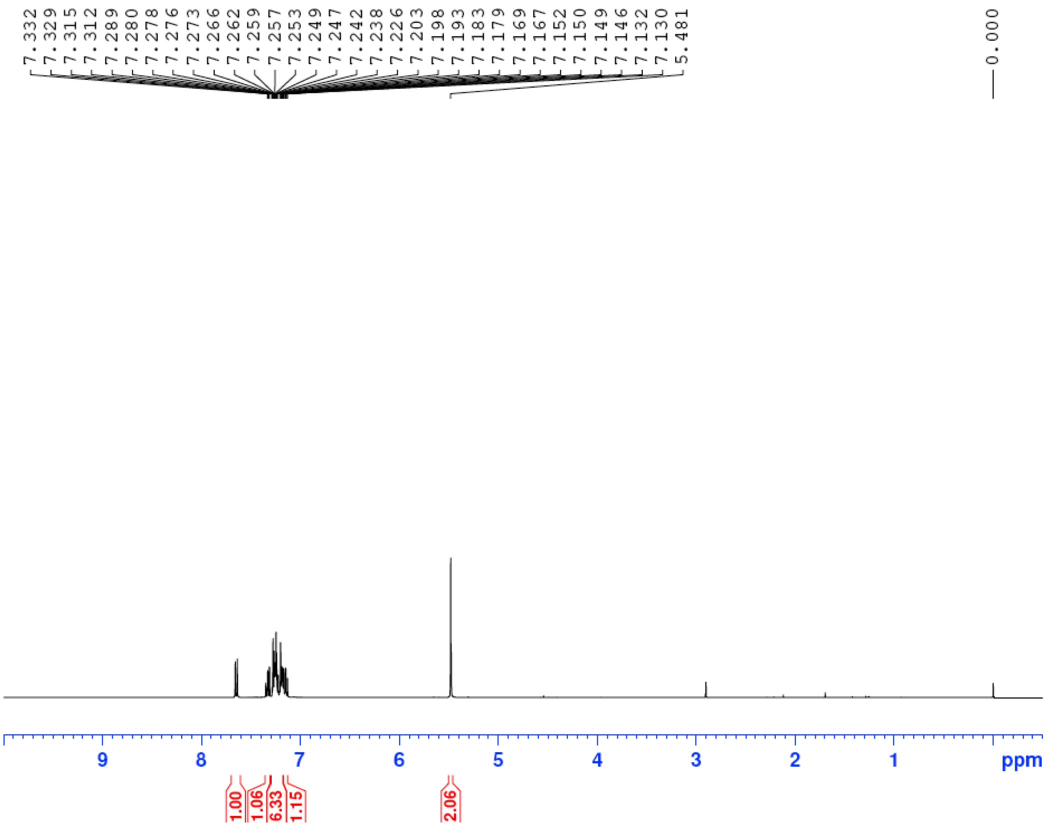
^{1}H and ^{13}C NMR of 1-benzyl-3-chloro-1*H*-indazole (**S6**)



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FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                       32
DW               62.400 usec
DE                 6.50 usec
TE                  298.2 K
D1           1.00000000 sec
TD0                       1

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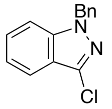

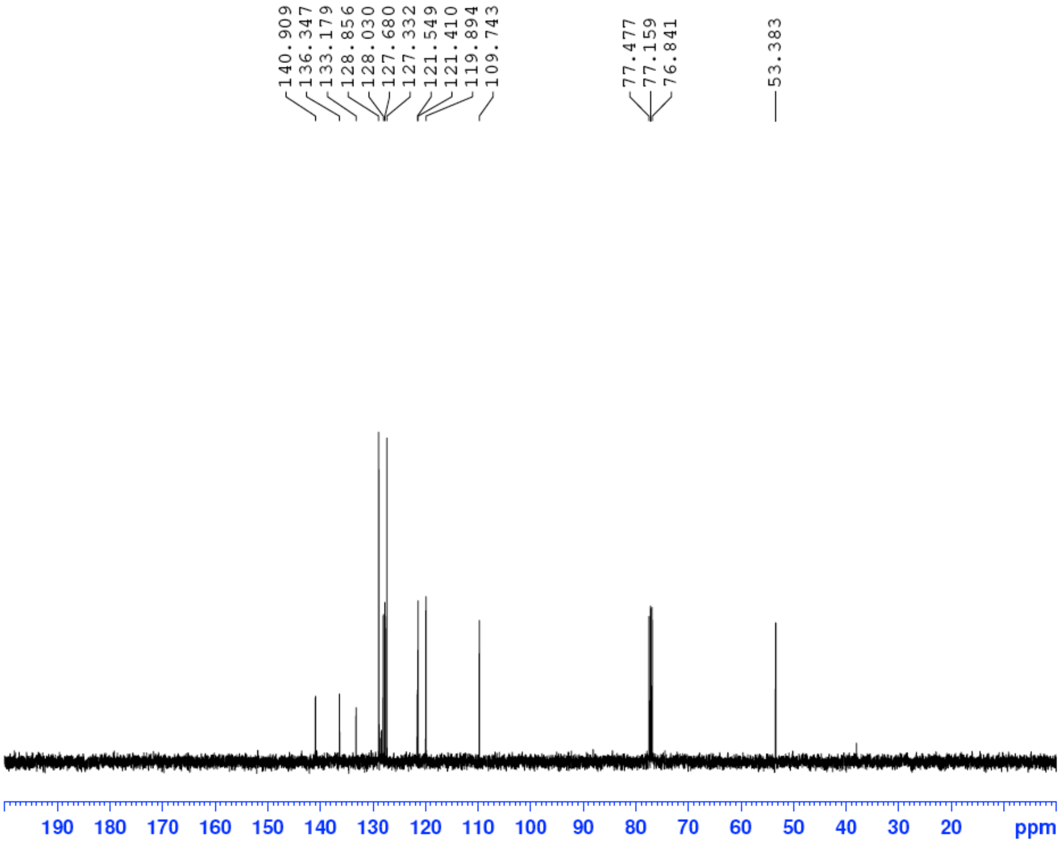

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TD                    65536
SOLVENT               CDCl3
NS                        2
DS                        4
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FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                      203
DW               20.800 usec
DE                 6.50 usec
TE                  298.2 K
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D11          0.03000000 sec
TD0                       1

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PLW13        0.21025001 W

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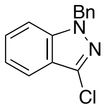
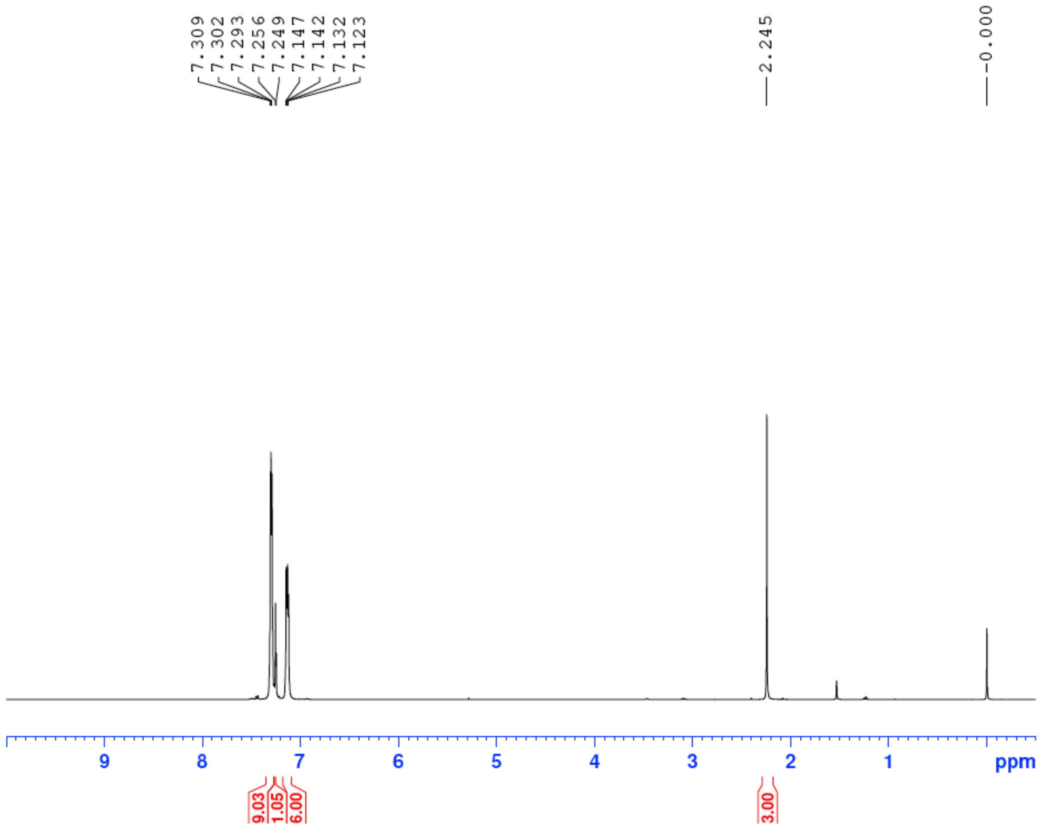


^{1}H and ^{13}C NMR of 4-bromo-3-methyl-1-trityl-1*H*-pyrazole (**S7)**



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DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                    144
DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

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NUC1                   1H
P1                  14.50 usec
PLW1          10.00000000 W

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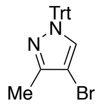

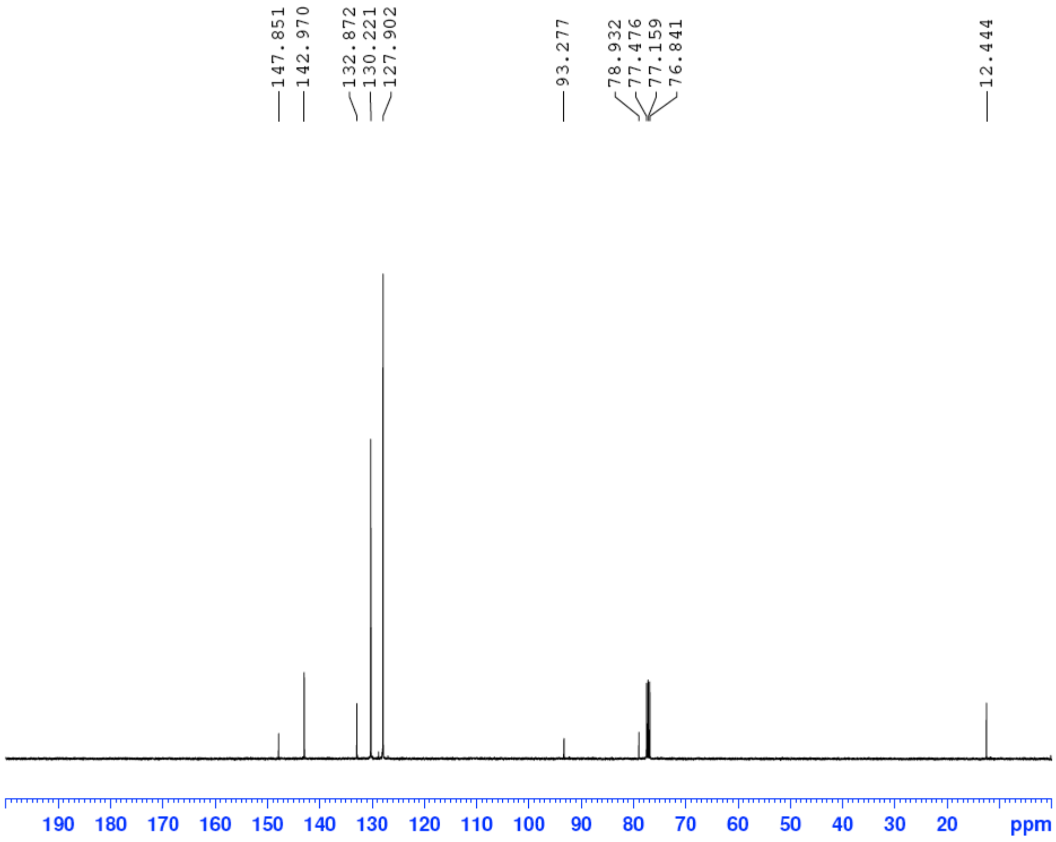

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FIDRES           0.366798 Hz
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RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
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======== CHANNEL f2 ========
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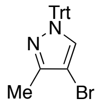
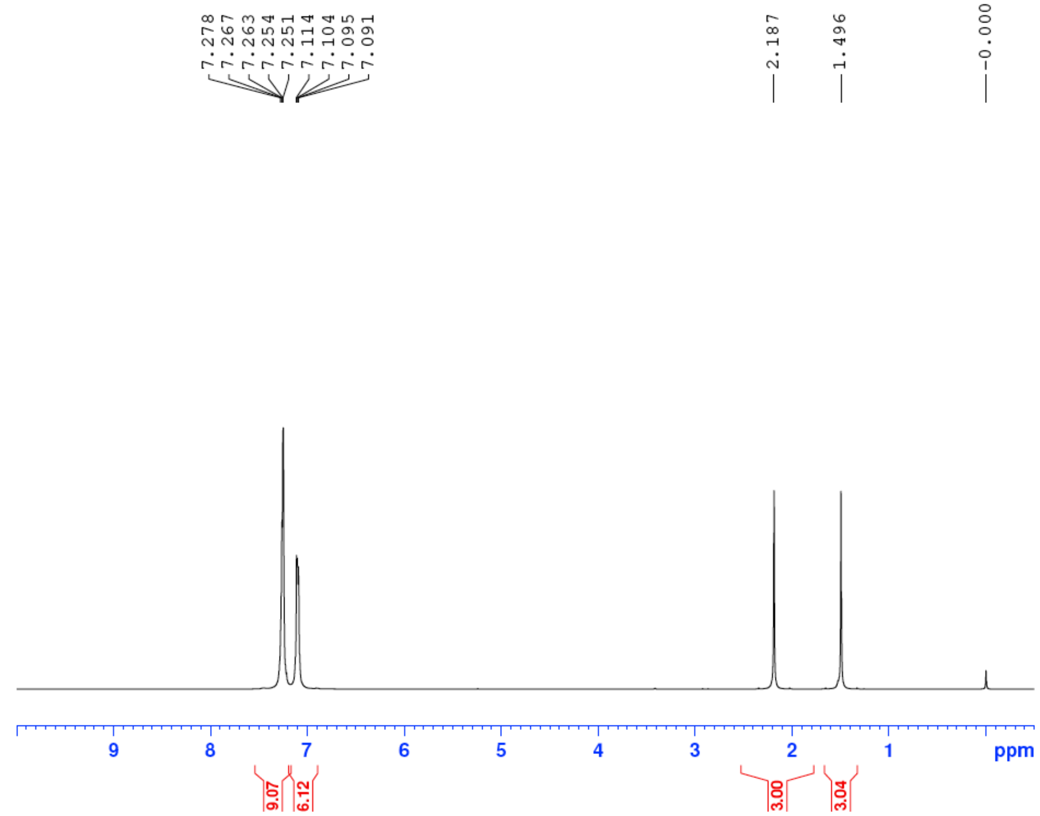


^{1}H and ^{13}C NMR of 4-bromo-3,5-dimethyl-1-trityl-1*H*-pyrazole (**S8**)



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FIDRES           0.122266 Hz
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DW                 62.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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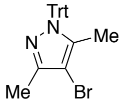

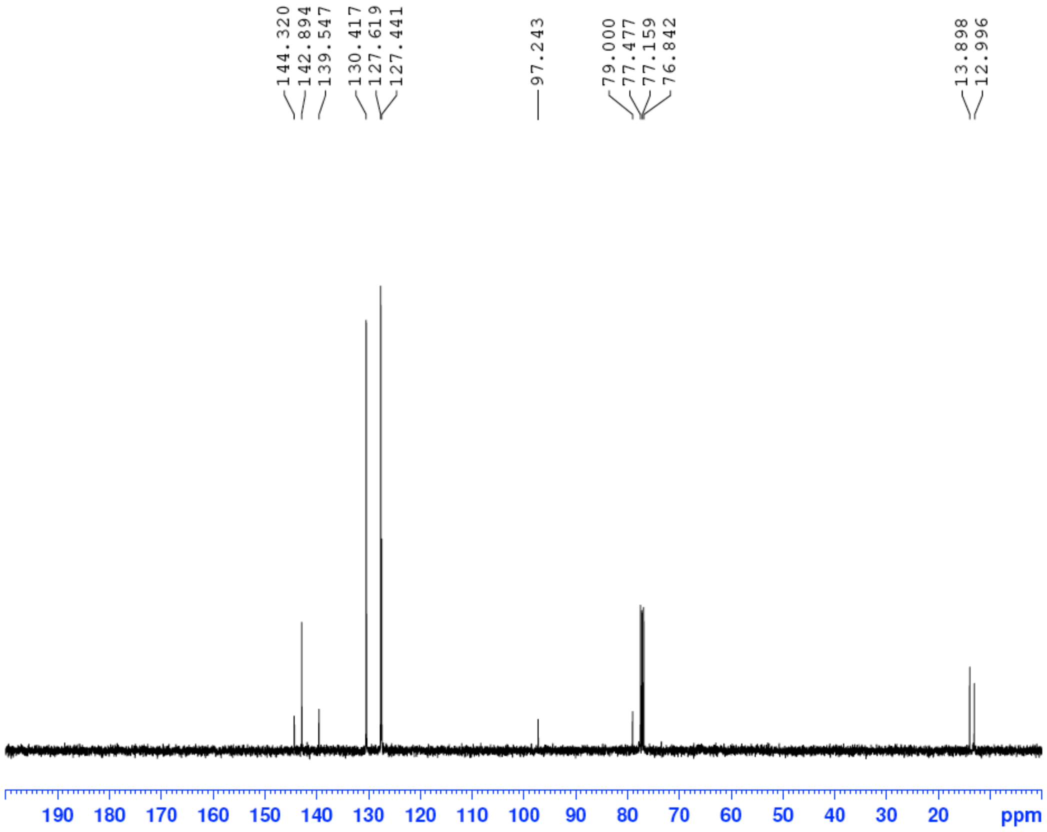

```
Current Data Parameters
NAME     CWC-VI-60-SM (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121121
Time                14.02
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     12
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                 198.22
DW                 20.800 usec
DE                   6.50 usec
TE                  298.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          44.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          10.00000000 W
PLW12          0.25957000 W
PLW13          0.21025001 W

F2 - Processing parameters
SI                  32768
SF            100.6127611 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
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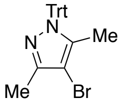
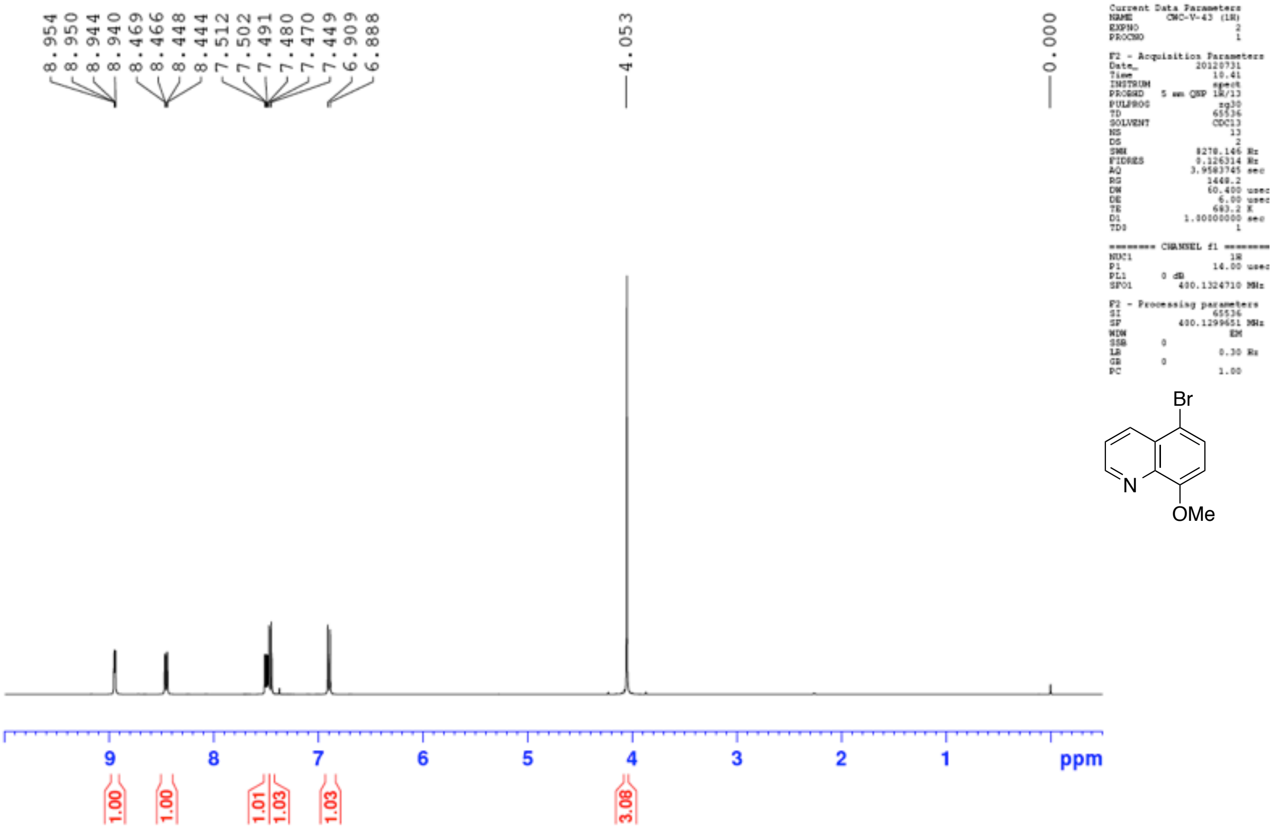


^{1}H and ^{13}C NMR of **5-chloro-8-methoxyquinoline** (S9)

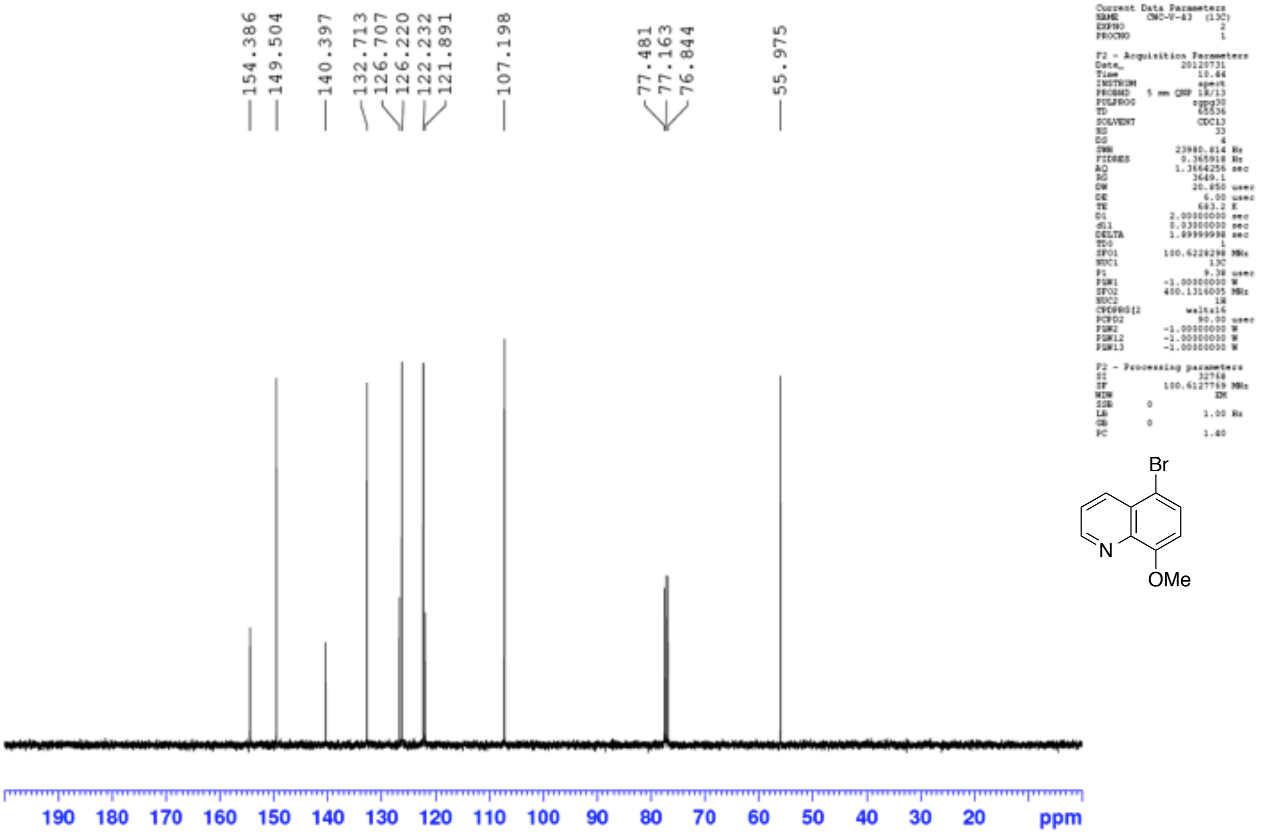


```
Current Data Parameters
NAME        CMC-V-43 (1H)
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120731
Time                10.41
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     13
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                 1448.2
DW                 60.400 usec
DE                   6.00 usec
TE                  683.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.00 usec
PL1        0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1299651 MHz
WDW                    EM
SSB        0
LB                   0.30 Hz
GB         0
PC                   1.00
```

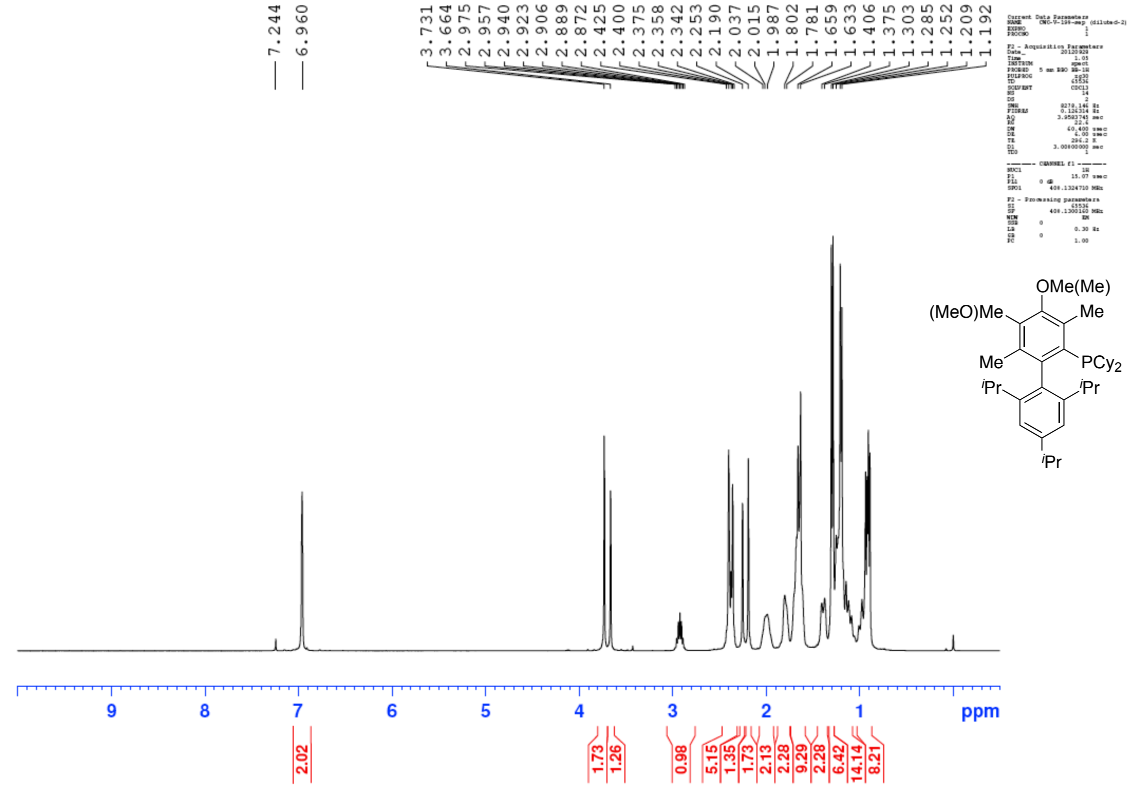


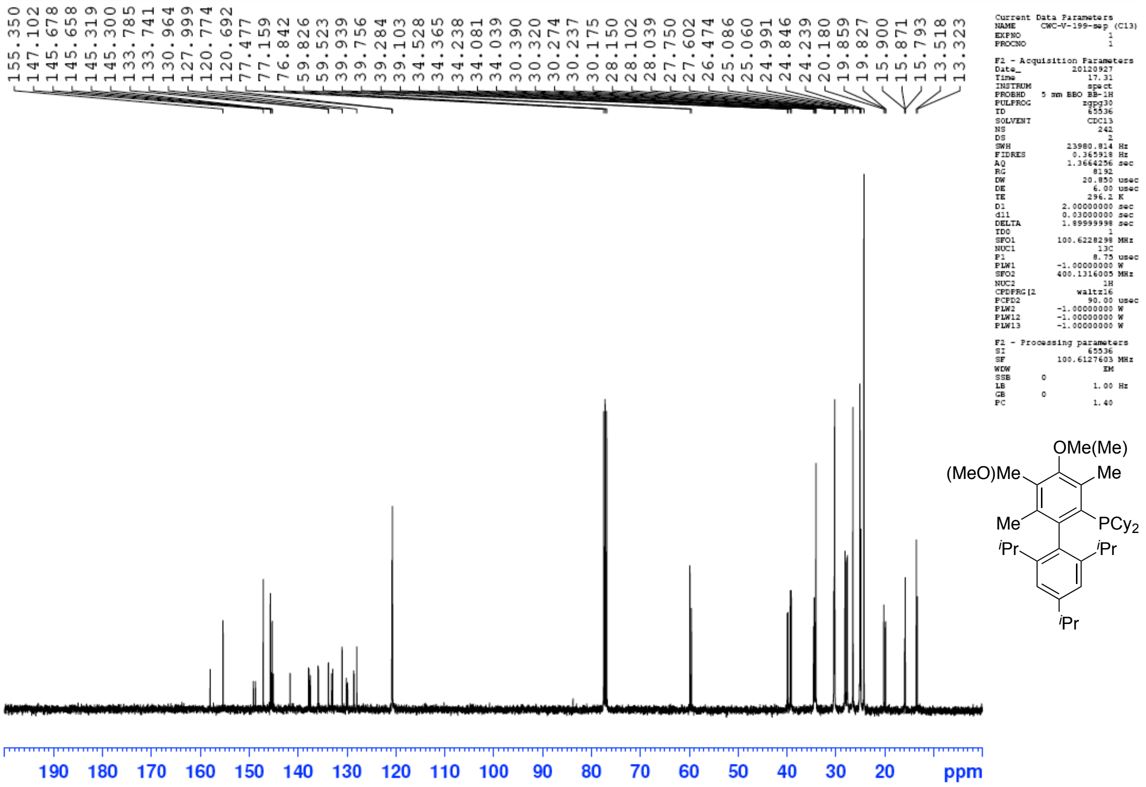
```
Current Data Parameters
NAME        CMC-V-43  (13C)
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120731
Time                10.44
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     33
DS                      4
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664256 sec
RG                 3649.1
DW                 20.850 usec
DE                   6.00 usec
TE                  683.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
SFO1          100.6228298 MHz
NUC1                  13C
P1                   9.38 usec
PLW1          -1.00000000 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

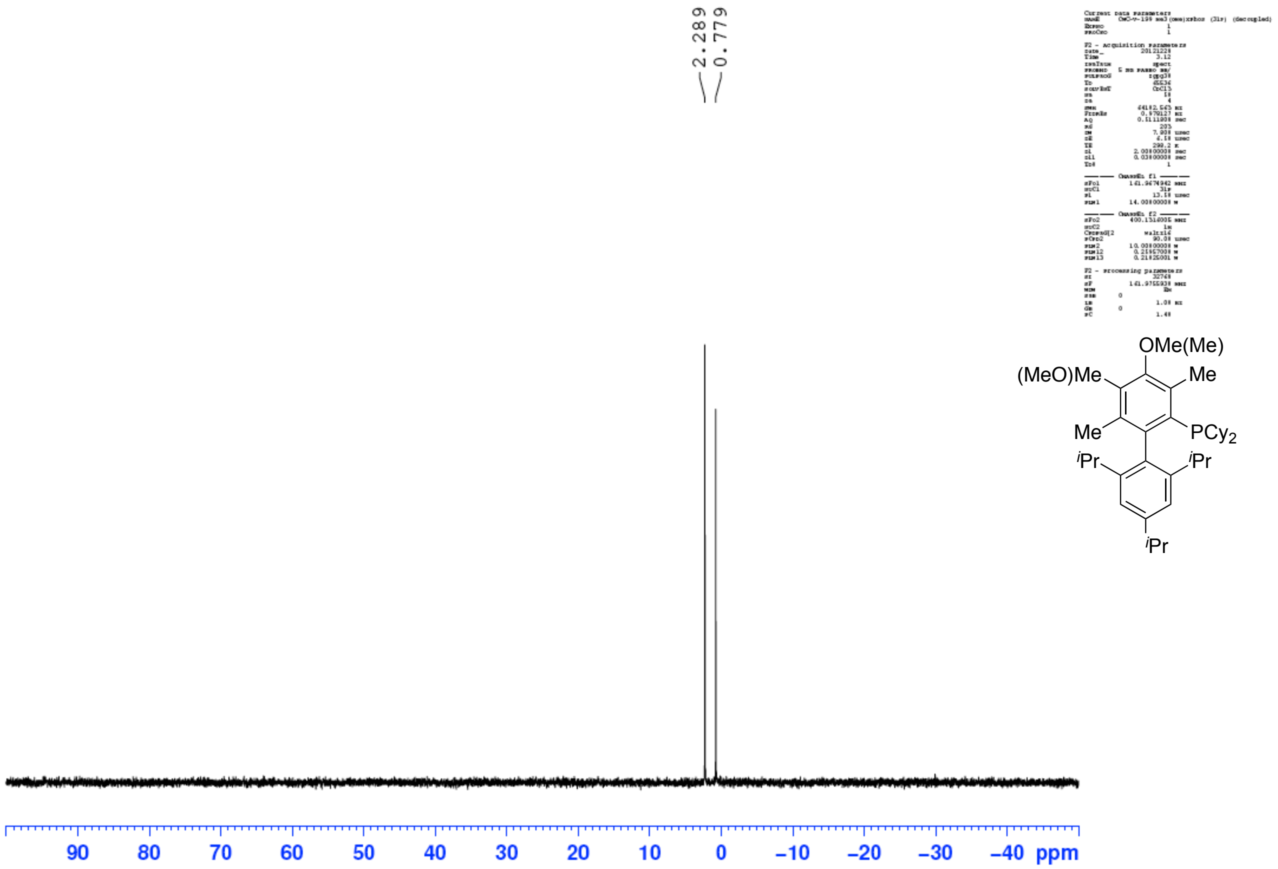
F2 - Processing parameters
SI                  32768
SF            100.6127769 MHz
WDW                    EM
SSB        0
LB                   1.00 Hz
GB         0
PC                   1.40
```

^{1}H and ^{13}C NMR of Dicyclohexyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Dicyclohexyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L6**)

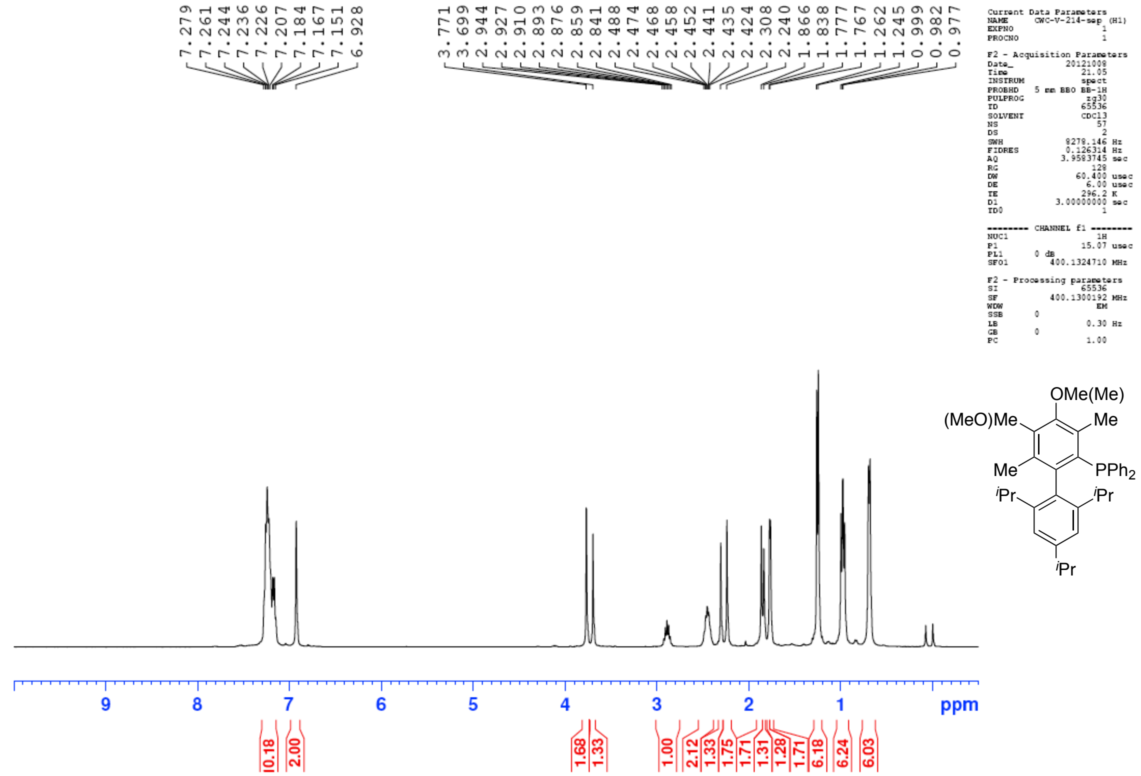




^{31}P NMR of Dicyclohexyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Dicyclohexyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L6**)



^{1}H and ^{13}C NMR of diphenyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine and diphenyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L7**)

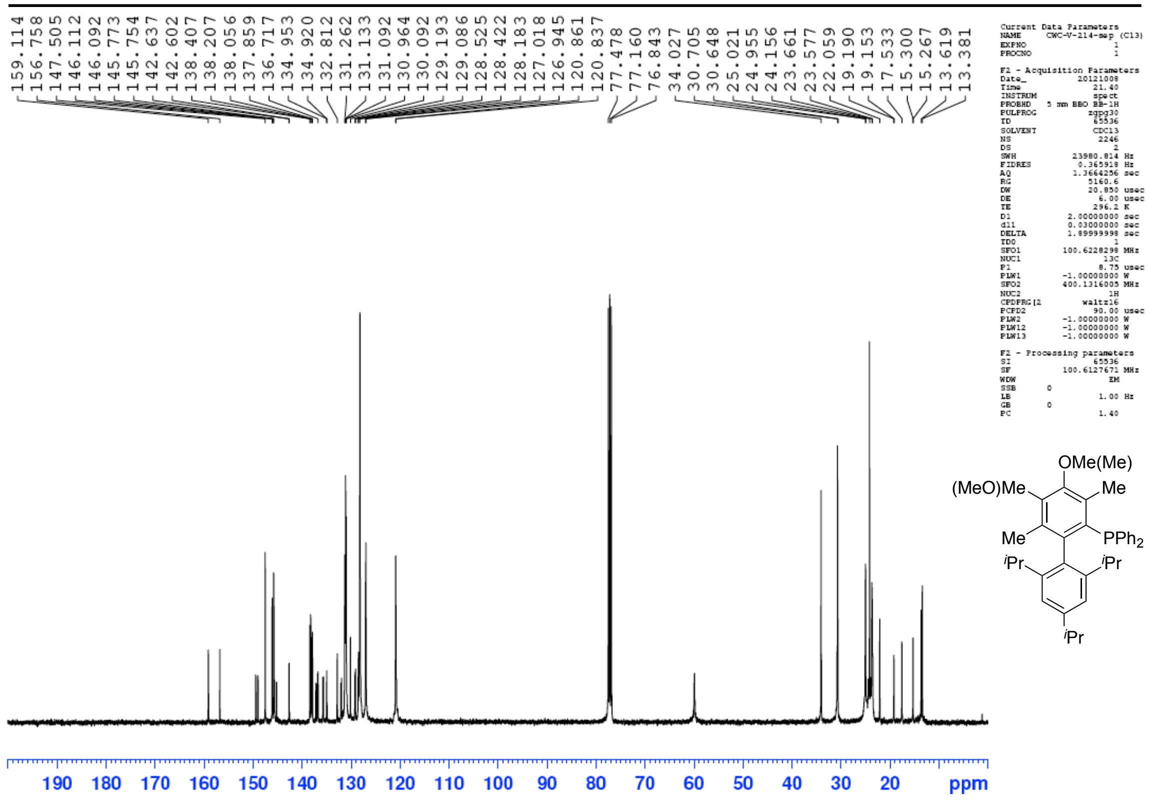


```
Current Data Parameters
NAME      CWC-V-214-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121008
Time                21.05
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     57
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                    128
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             3.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1       0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300192 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

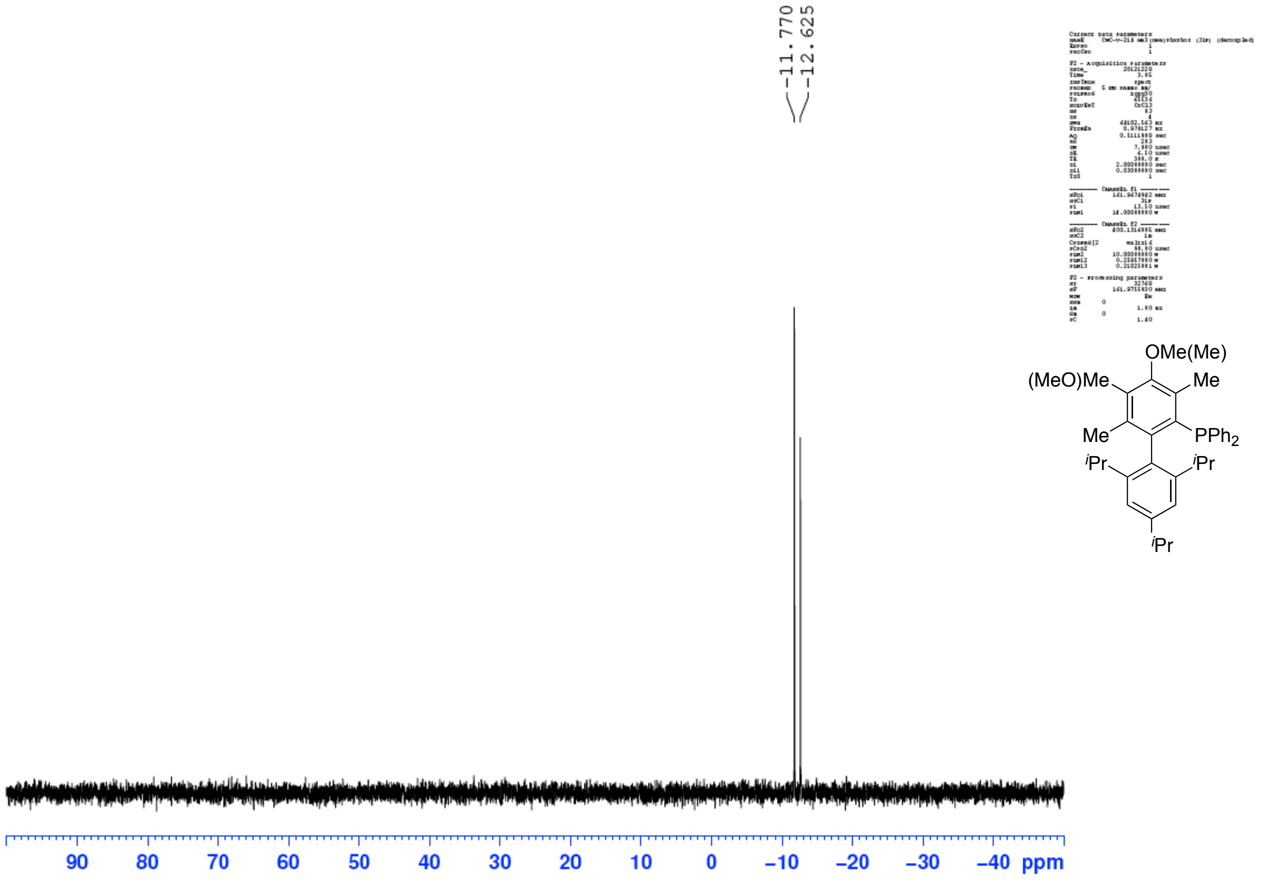


```
Current Data Parameters
NAME      CWC-V-214-sep (C13)
EXPNO                   1
PROCNO                  1

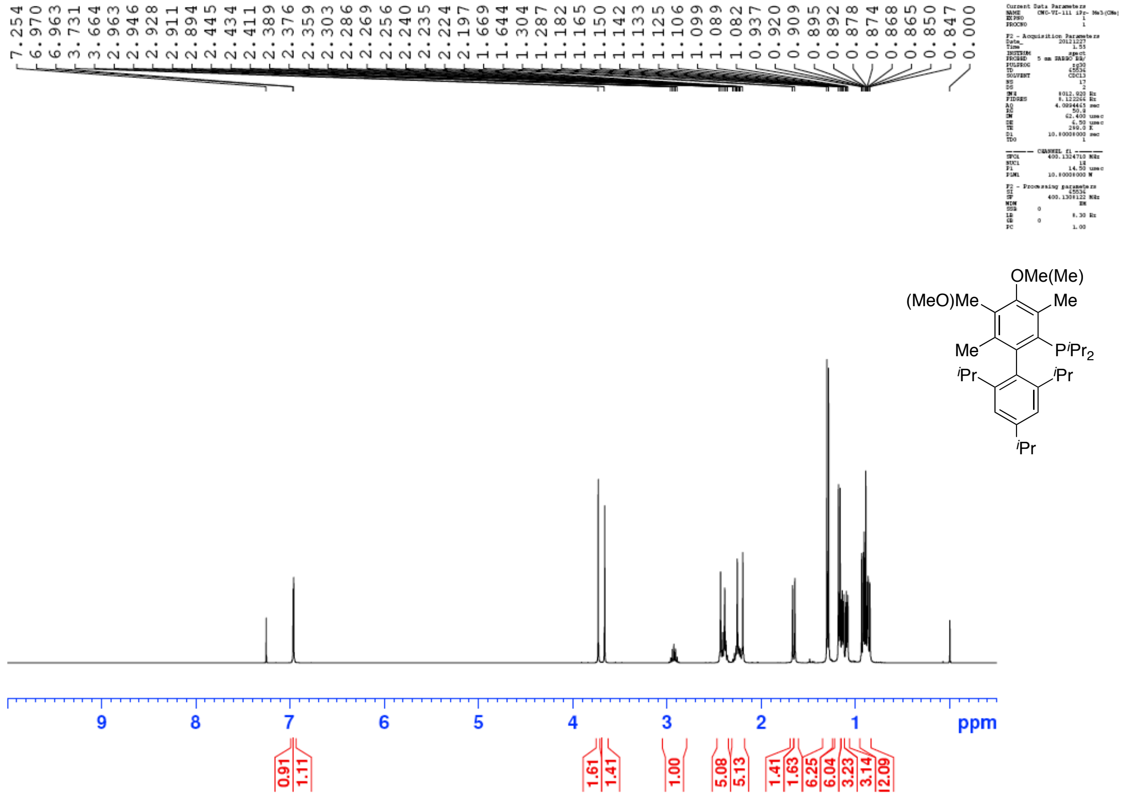
F2 - Acquisition Parameters
Date_            20121008
Time                21.40
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2246
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664256 sec
RG                 5160.6
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
SFO1          100.6228298 MHz
NUC1                  13C
P1                   8.75 usec
PLW1          -1.00000000 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

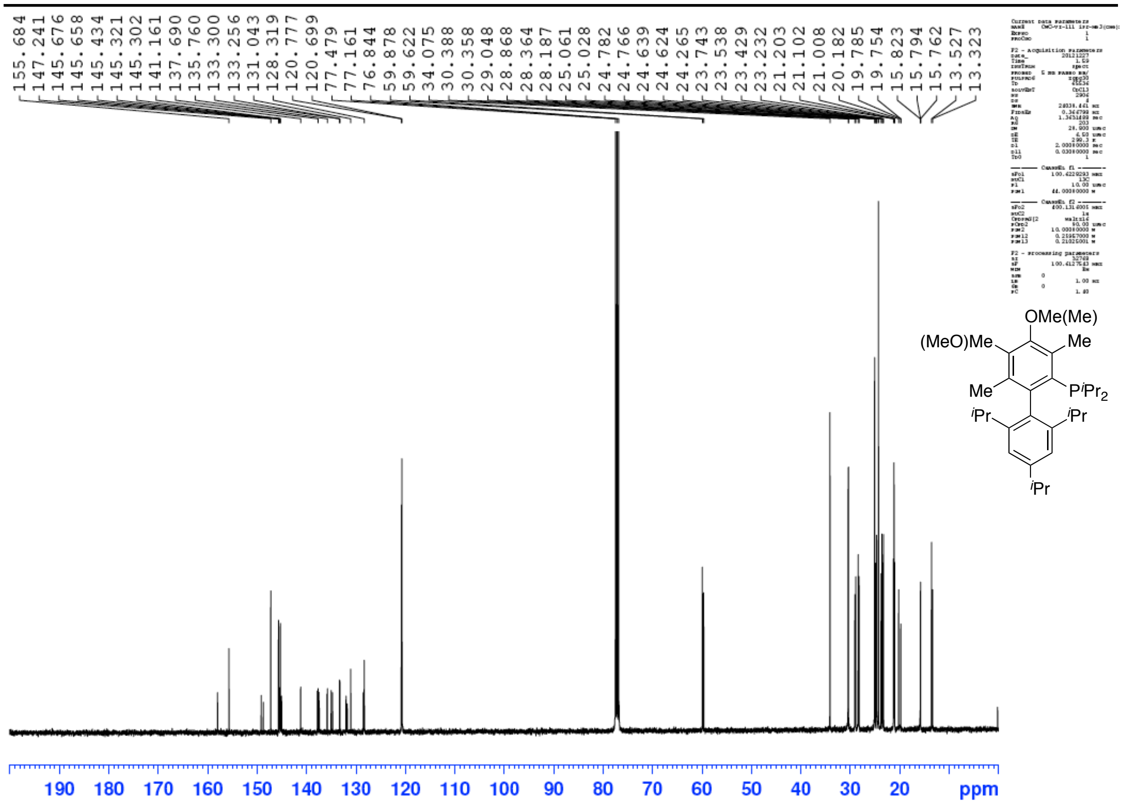
F2 - Processing parameters
SI                  65536
SF            100.6127671 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

^{31}P NMR of diphenyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine and diphenyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L7**)

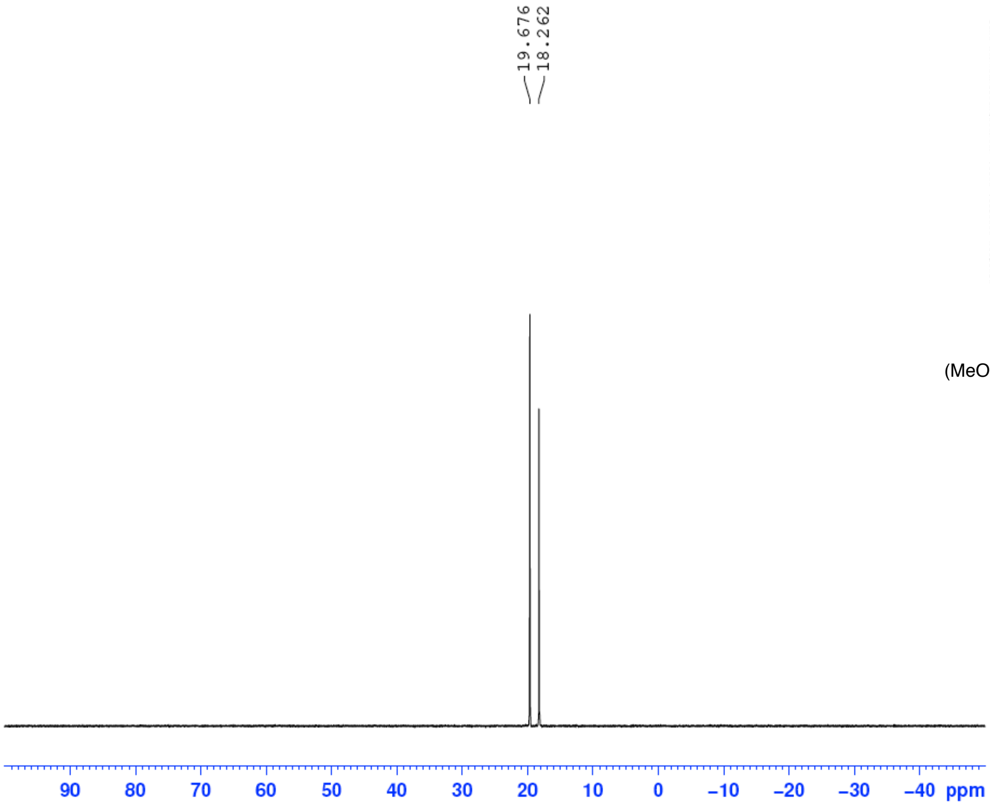


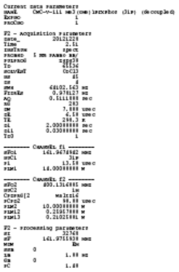
^{1}H and ^{13}C NMR of Diisopropyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Diisopropyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L8**)

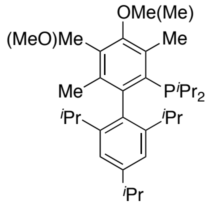




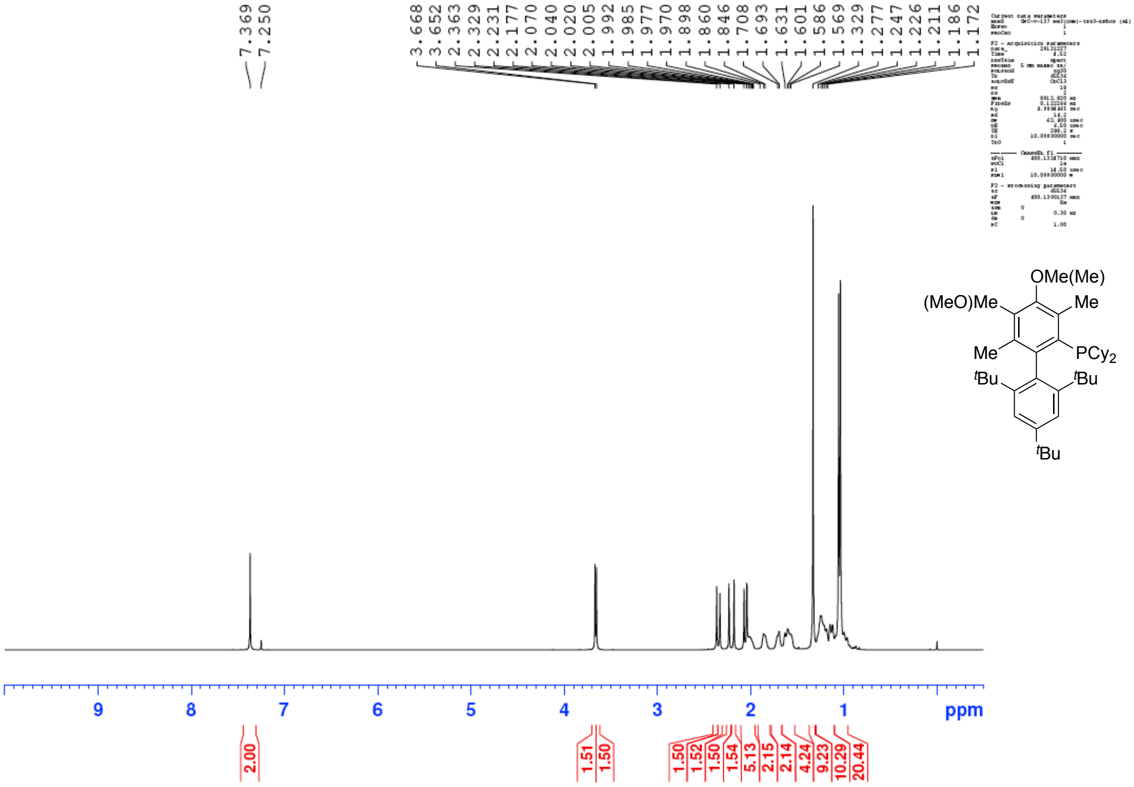
^{31}P NMR of Diisopropyl(2',4',6'-triisopropyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine / Diisopropyl(2',4',6'-triisopropyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L8**)

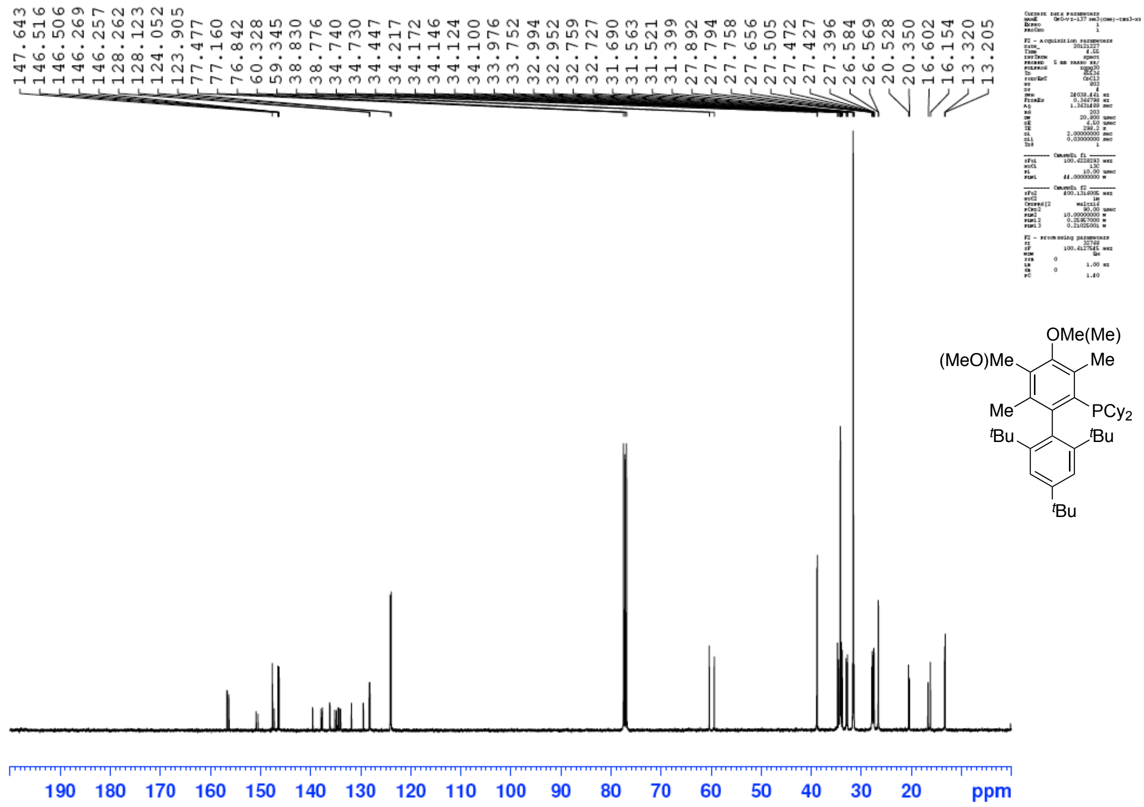




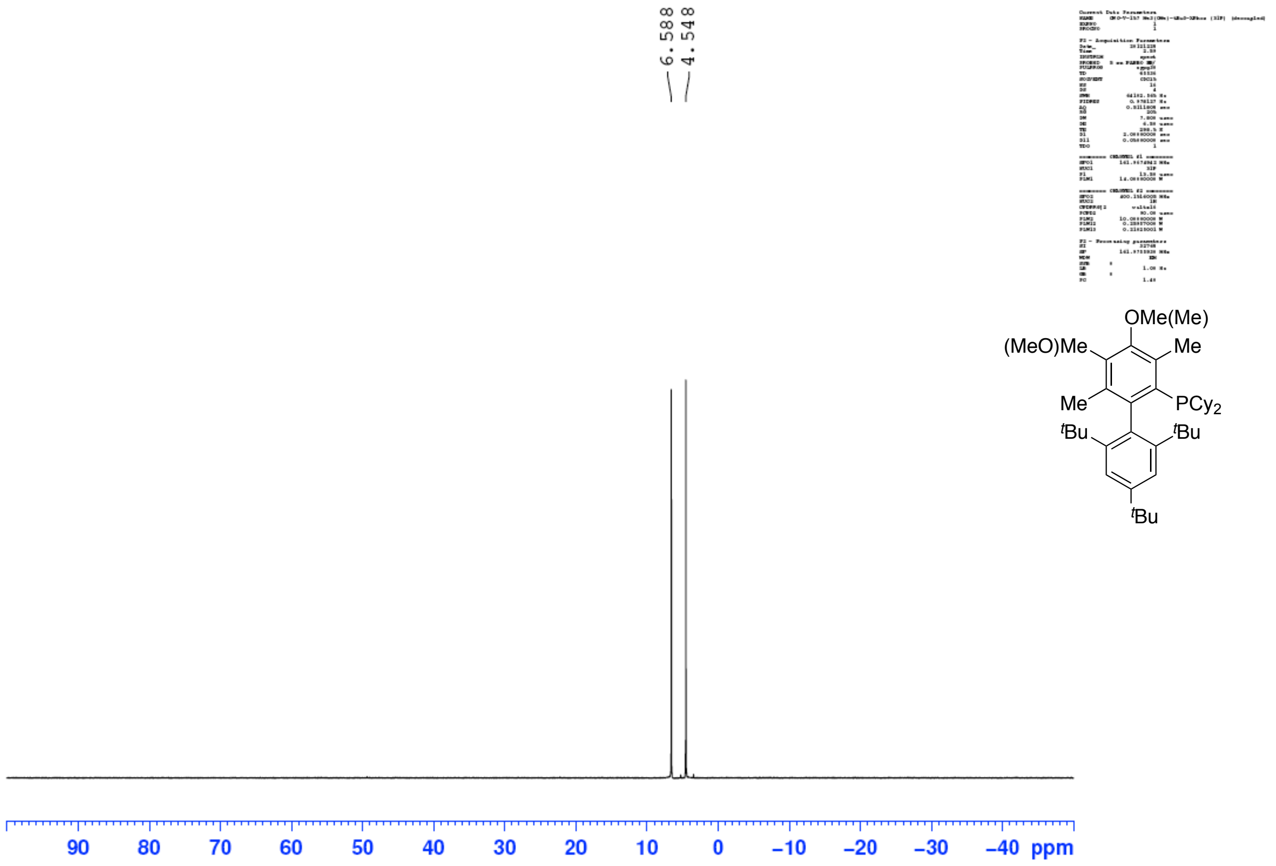


^{1}H and ^{13}C NMR of Dicyclohexyl(2',4',6'-tri-*tert*-butyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine and Dicyclohexyl(2',4',6'-tri-*tert*-butyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L9**)

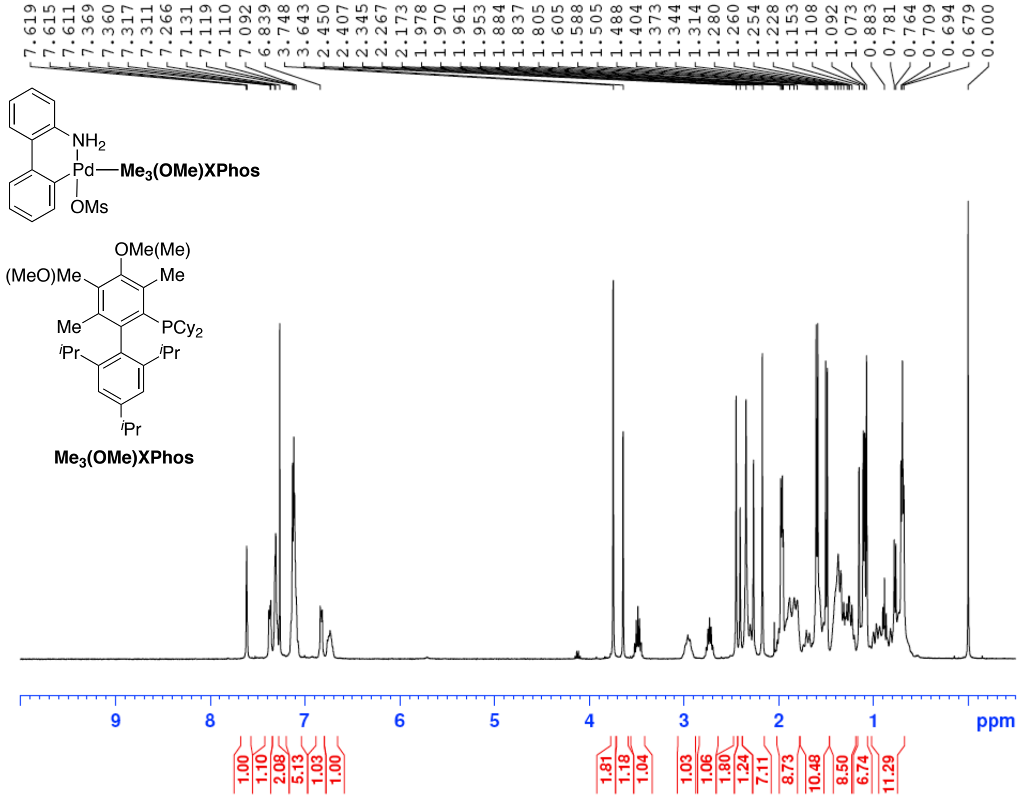




^{31}P NMR of Dicyclohexyl(2',4',6'-tri-*tert*-butyl-4-methoxy-3,5,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine and Dicyclohexyl(2',4',6'-tri-*tert*-butyl-5-methoxy-3,4,6-trimethyl-[1,1'-biphenyl]-2-yl)phosphine (**L9**)



^{1}H and ^{13}C NMR of Aminobiphenyl Palladacycle Precatalyst (**3a**)

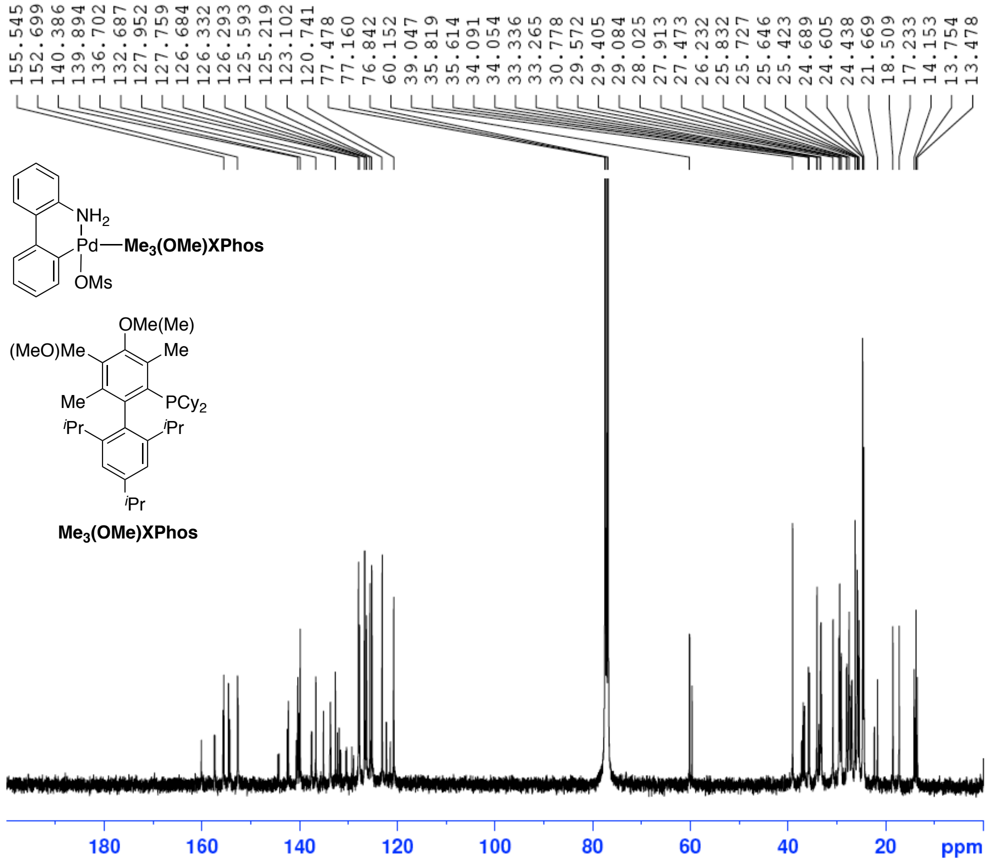


```
Current Data Parameters
NAME     CMC-V-190 (1H) (dilute-2)
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120923
Time               3.14
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9583745 sec
RG                203.2
DW               60.400 usec
DE                 6.00 usec
TE                296.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.07 usec
PL1      0 dB
SF01        400.1324710 MHz

F2 - Processing parameters
SI                65536
SF          400.1300067 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



```
Current Data Parameters
NAME     CWC-IV-228-dried (13C)
EXPNO                 1
PROCNO                1

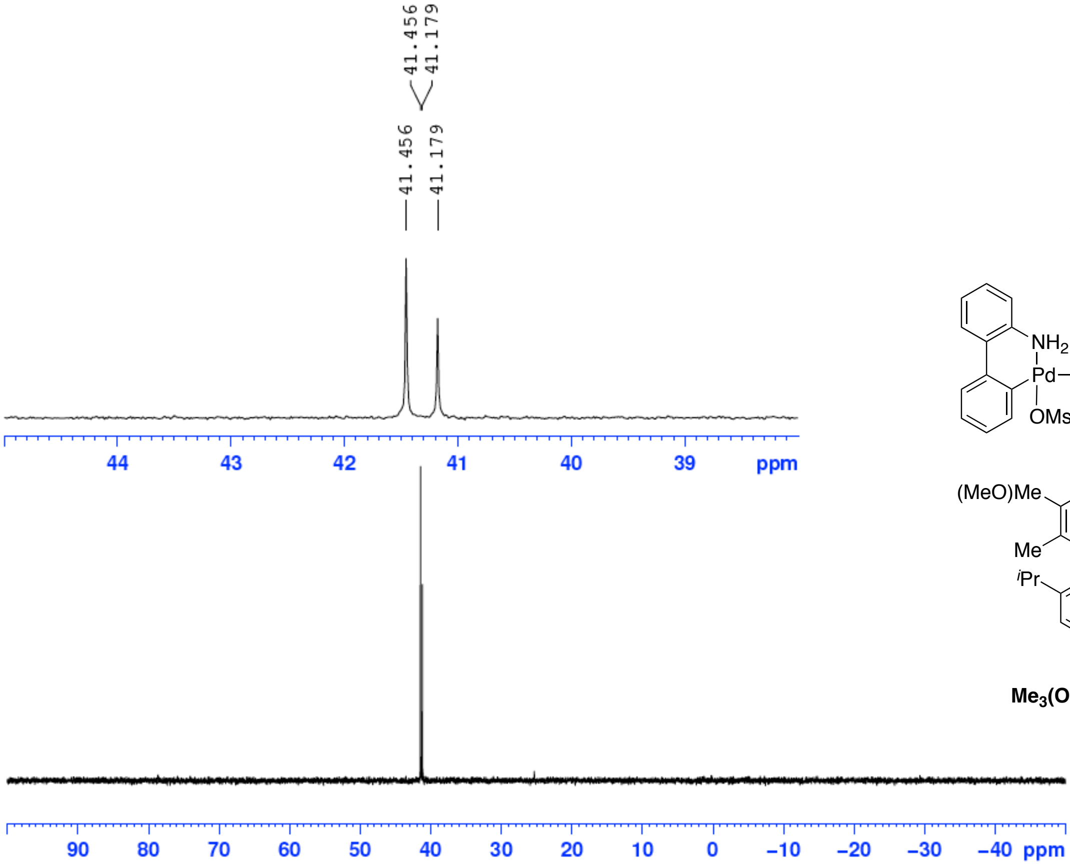
F2 - Acquisition Parameters
Date_          20120708
Time               1.31
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4781
DS                    2
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                 8192
DW               20.850 usec
DE                 6.00 usec
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

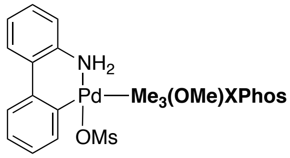
======== CHANNEL f1 ========
NUC1                13C
P1                 8.75 usec
PL1               -3.00 dB
SF01        100.6228298 MHz

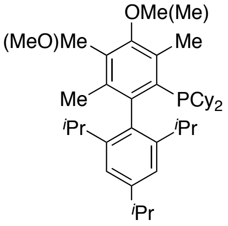
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              14.52 dB
PL13              18.00 dB
SF02        400.1316005 MHz

F2 - Processing parameters
SI                65536
SF          100.6127662 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{31}P NMR of Aminobiphenyl Palladacycle Precatalyst (**3a**)

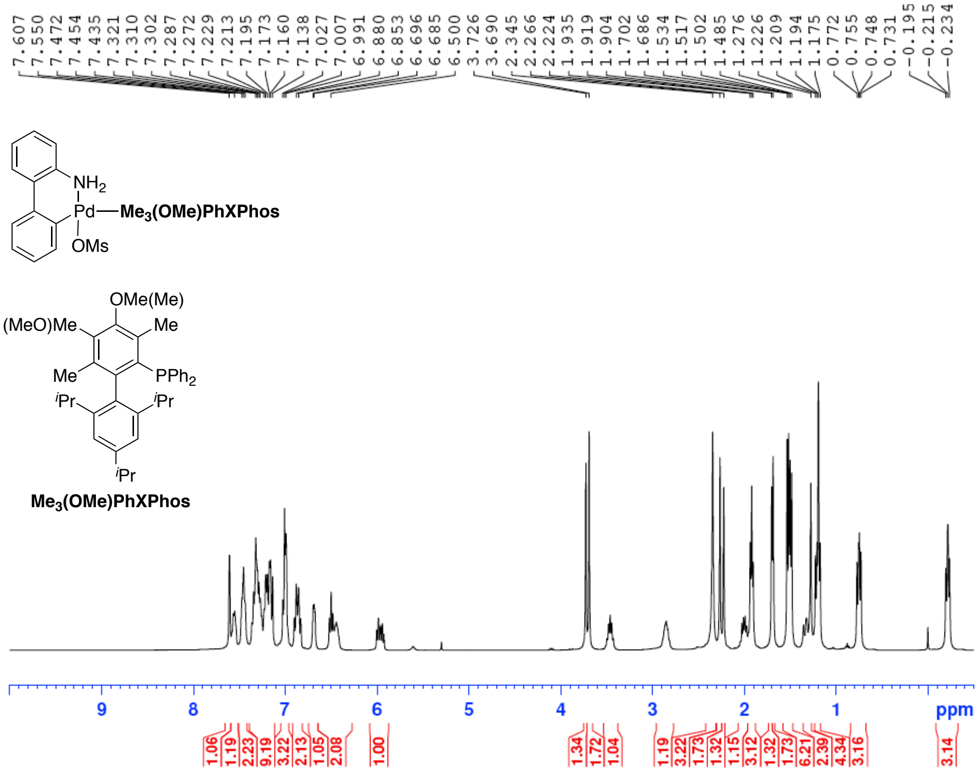






Me$_3$(OMe)XPhos

^{1}H and ^{13}C NMR of Aminobiphenyl Palladacycle Precatalyst (**3b**)

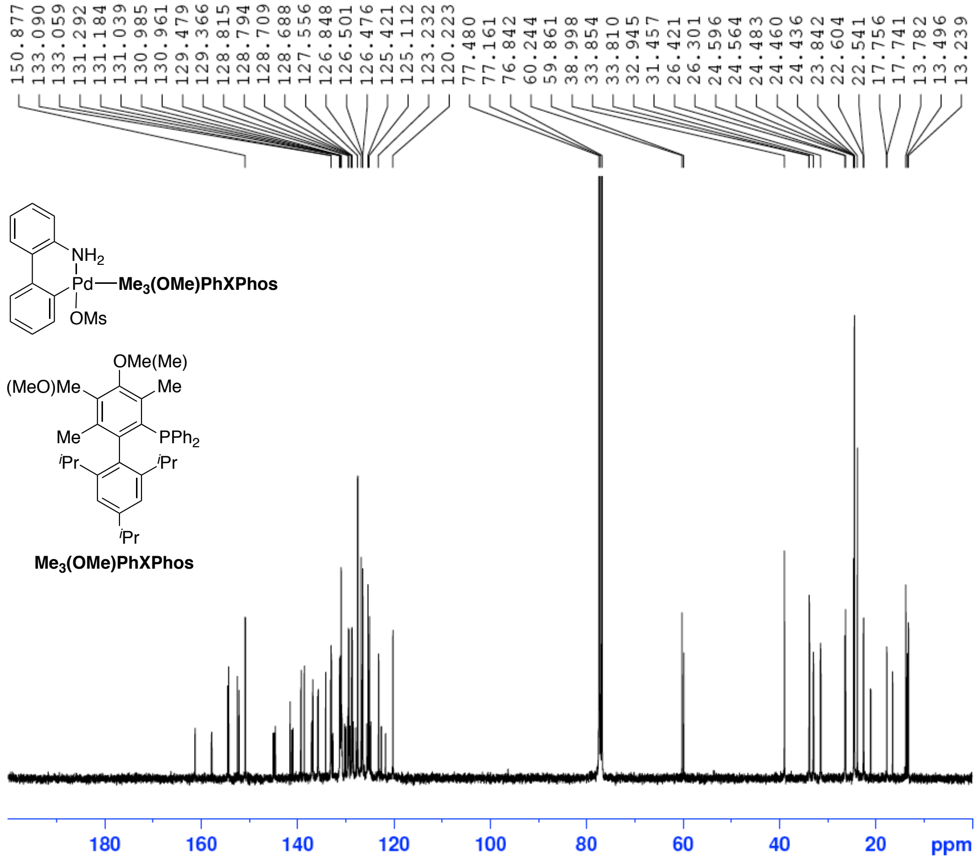


```
Current Data Parameters
NAME     CWC-V-159-sep (1H)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120923
Time                 5.08
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     52
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                   35.9
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1      0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1299862 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



```
Current Data Parameters
NAME     CWC-V-159-sep (13C)
EXPNO                   1
PROCNO                  1

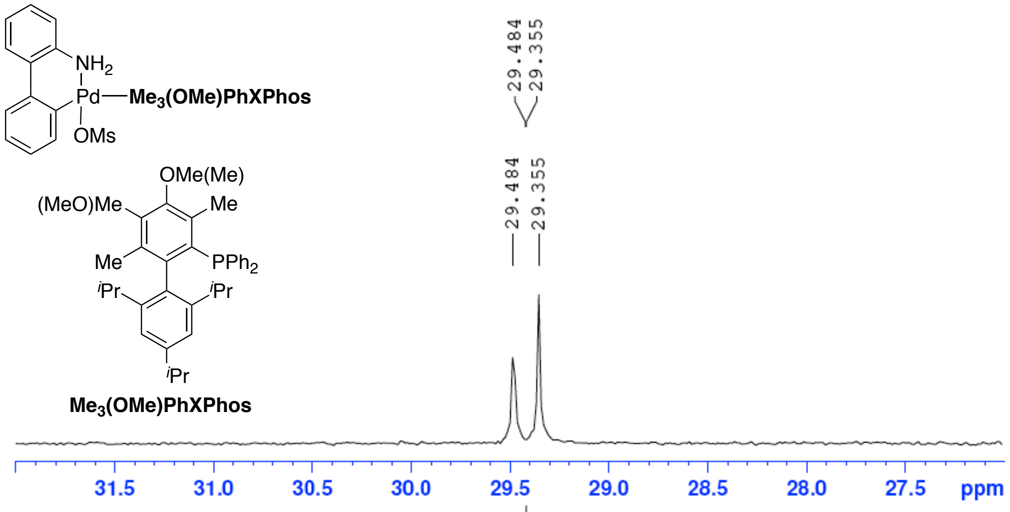
F2 - Acquisition Parameters
Date_            20120923
Time                 5.13
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   3019
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

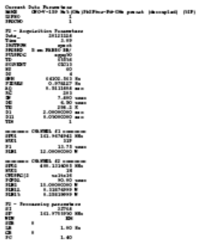
======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

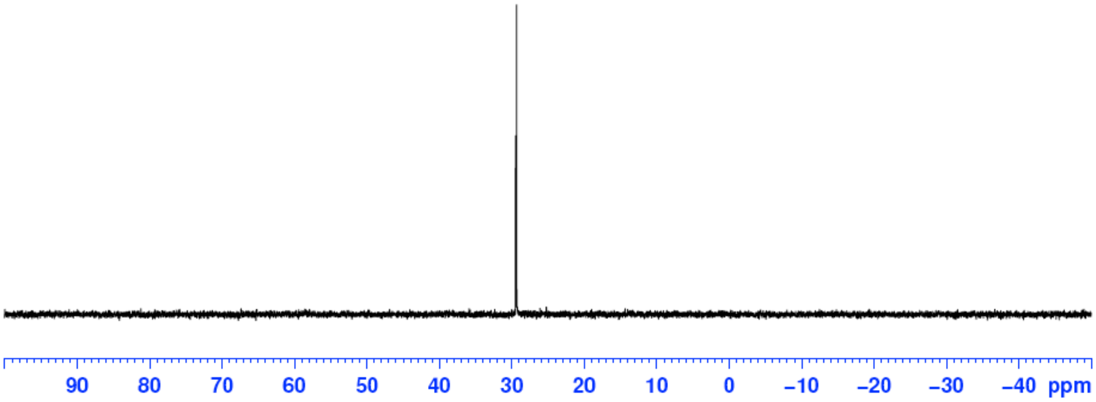
======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127731 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

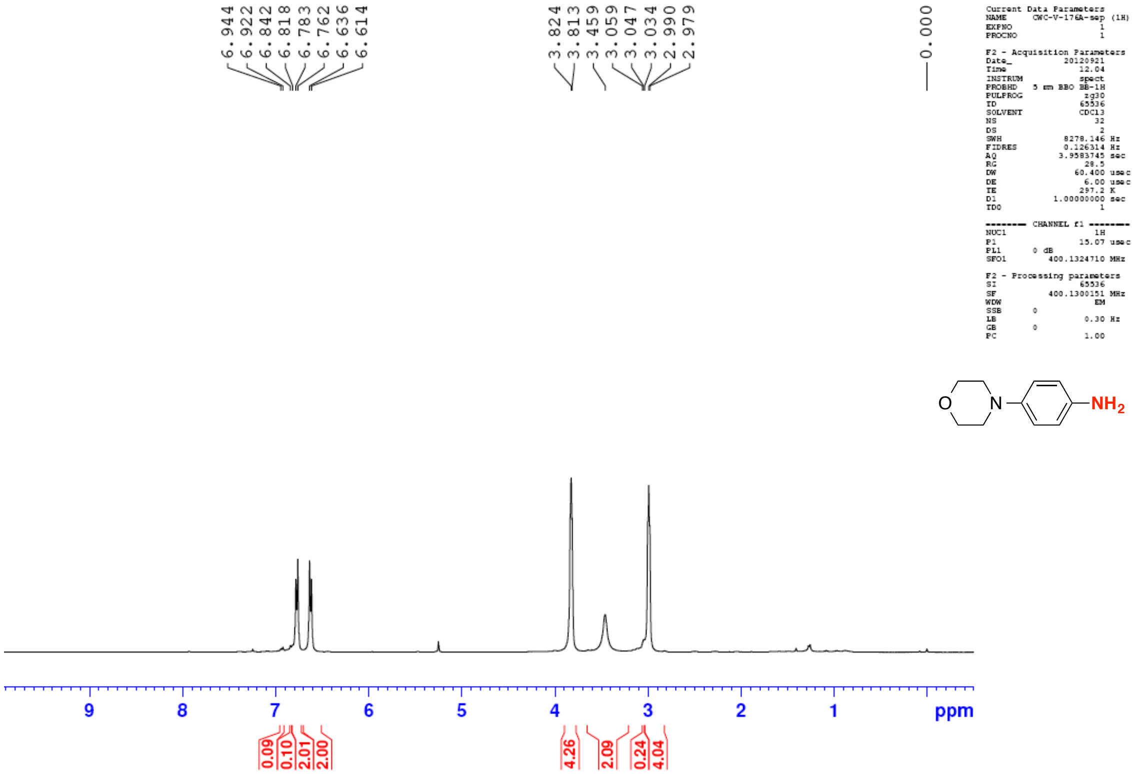
^{31}P NMR of Aminobiphenyl Palladacycle Precatalyst (**3b**)







^{1}H and ^{13}C NMR of 4-Morpholinoaniline (**4a**)

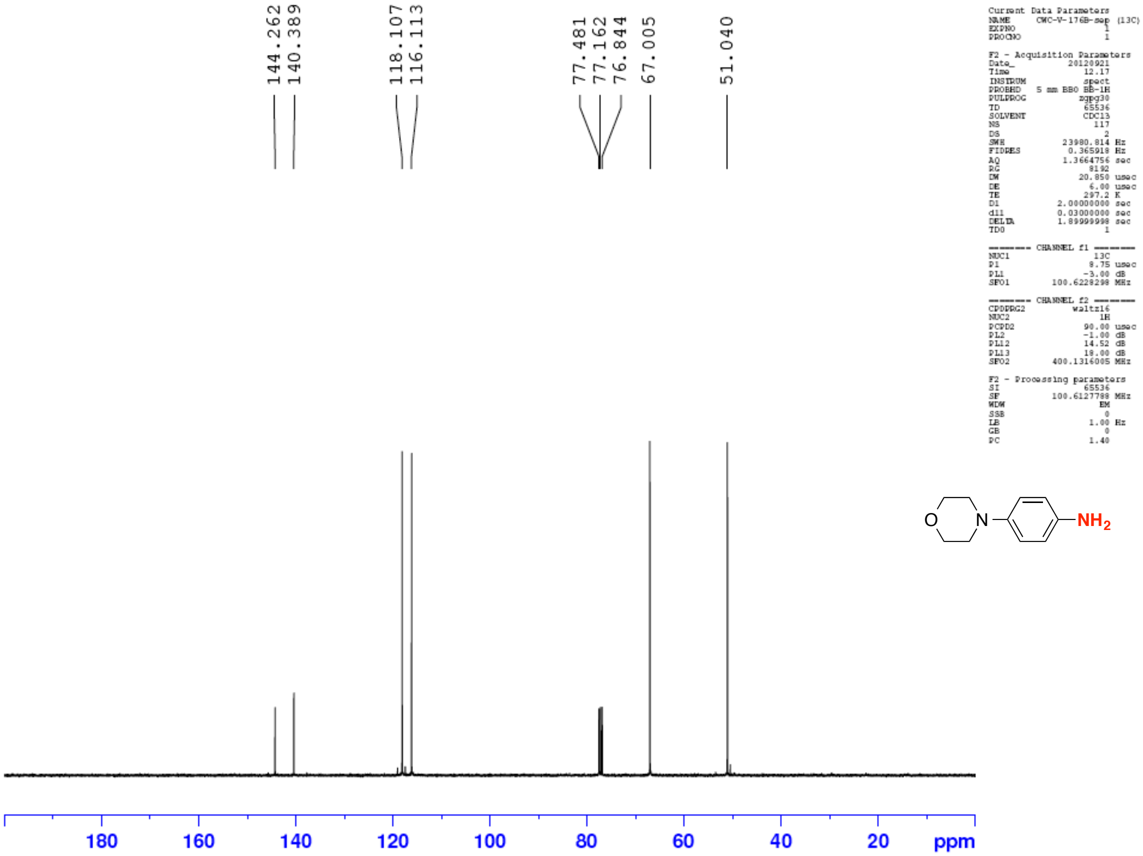


```
Current Data Parameters
NAME       CWC-V-176A-sep (1H)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120921
Time                 12.04
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9583745 sec
RG                    28.5
DW              60.400 usec
DE                6.00 usec
TE               297.2 K
D1          1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1               15.07 usec
PL1       0 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF         400.1300151 MHz
WDW                     EM
SSB       0
LB                 0.30 Hz
GB        0
PC                    1.00
```



```
Current Data Parameters
NAME       CWC-V-176B-sep (13C)
EXPNO                    1
PROCNO                   1

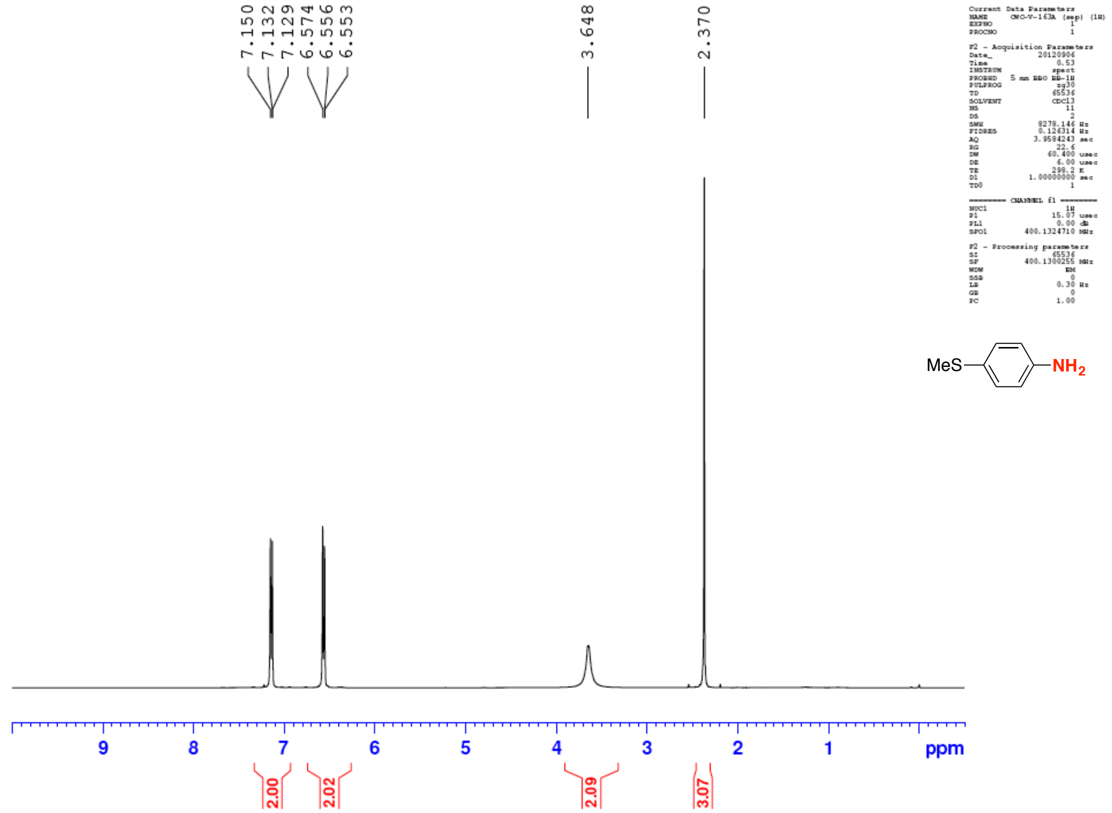
F2 - Acquisition Parameters
Date_             20120921
Time                 12.17
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     117
DS                       2
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG                    8192
DW              20.850 usec
DE                6.00 usec
TE               297.2 K
D1          2.00000000 sec
d11         0.03000000 sec
DELTA       1.89999998 sec
TD0                      1

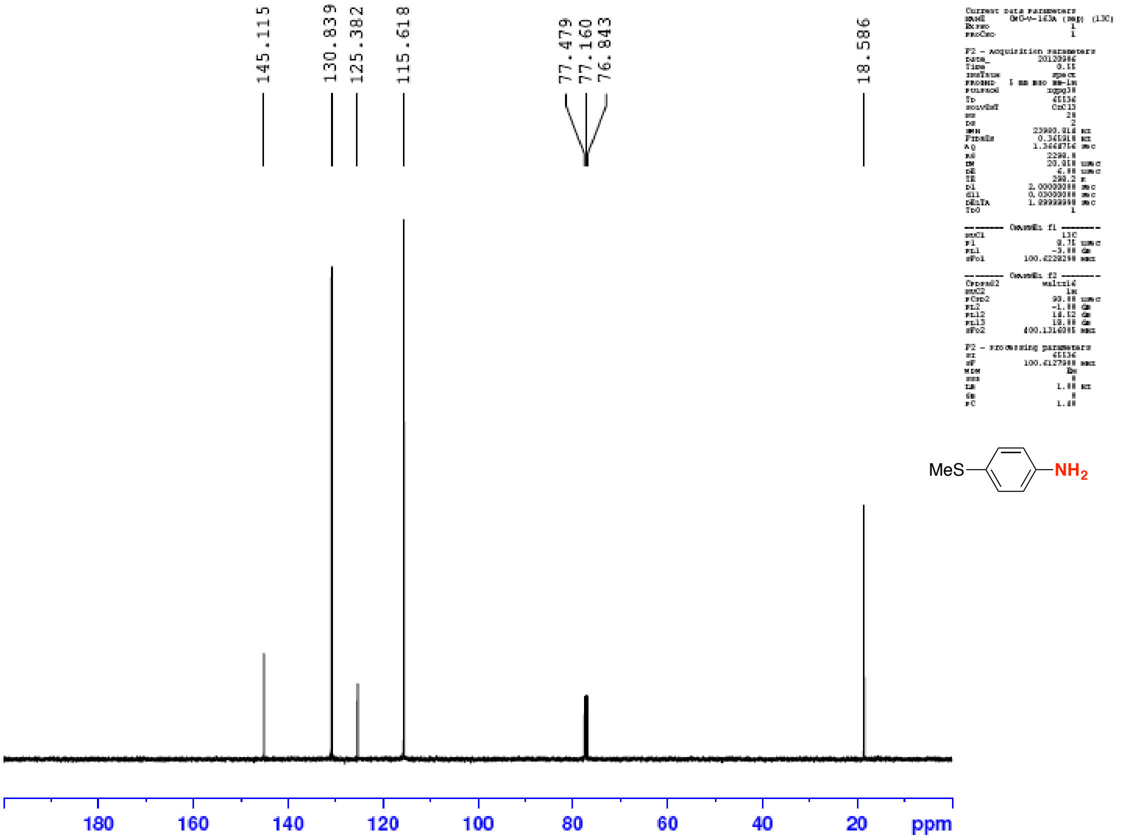
======== CHANNEL f1 ========
NUC1                   13C
P1                8.75 usec
PL1              -3.00 dB
SFO1       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            90.00 usec
PL2              -1.00 dB
PL12             14.52 dB
PL13             18.00 dB
SFO2       400.1316005 MHz

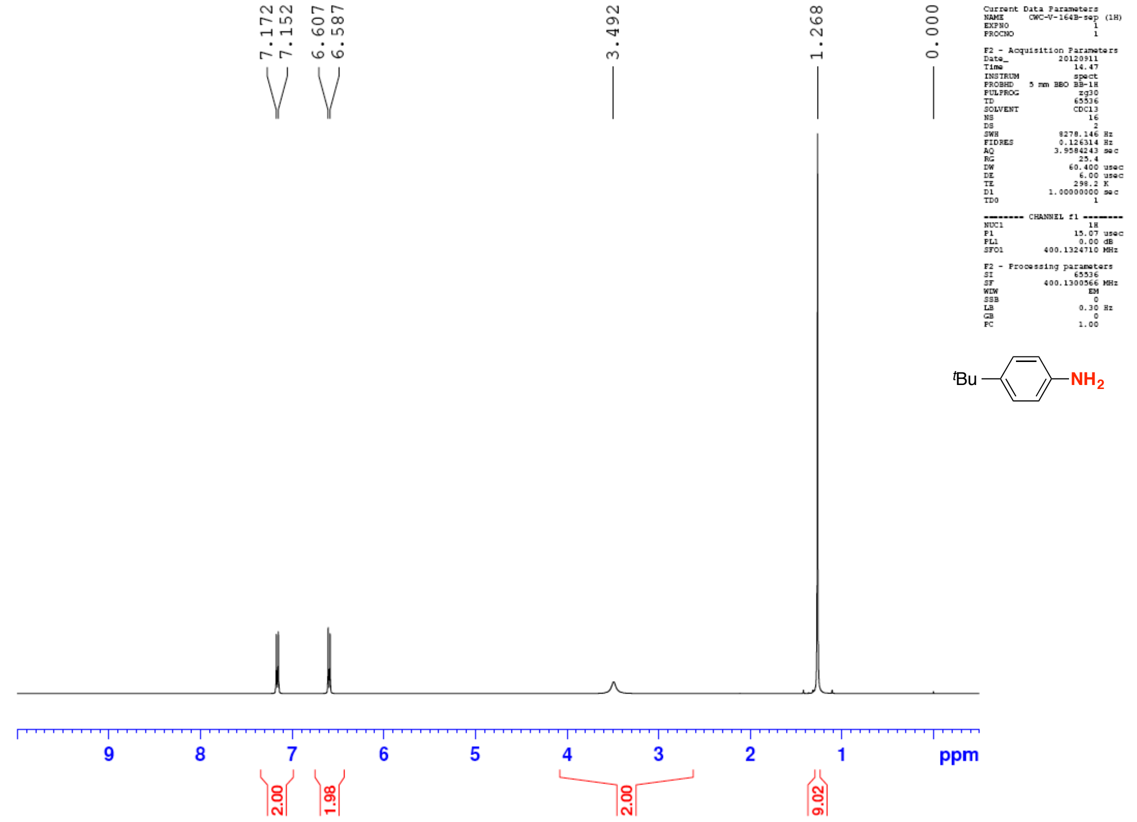
F2 - Processing parameters
SI                   65536
SF         100.6127788 MHz
WDW                     EM
SSB                      0
LB                 1.00 Hz
GB                       0
PC                    1.40
```

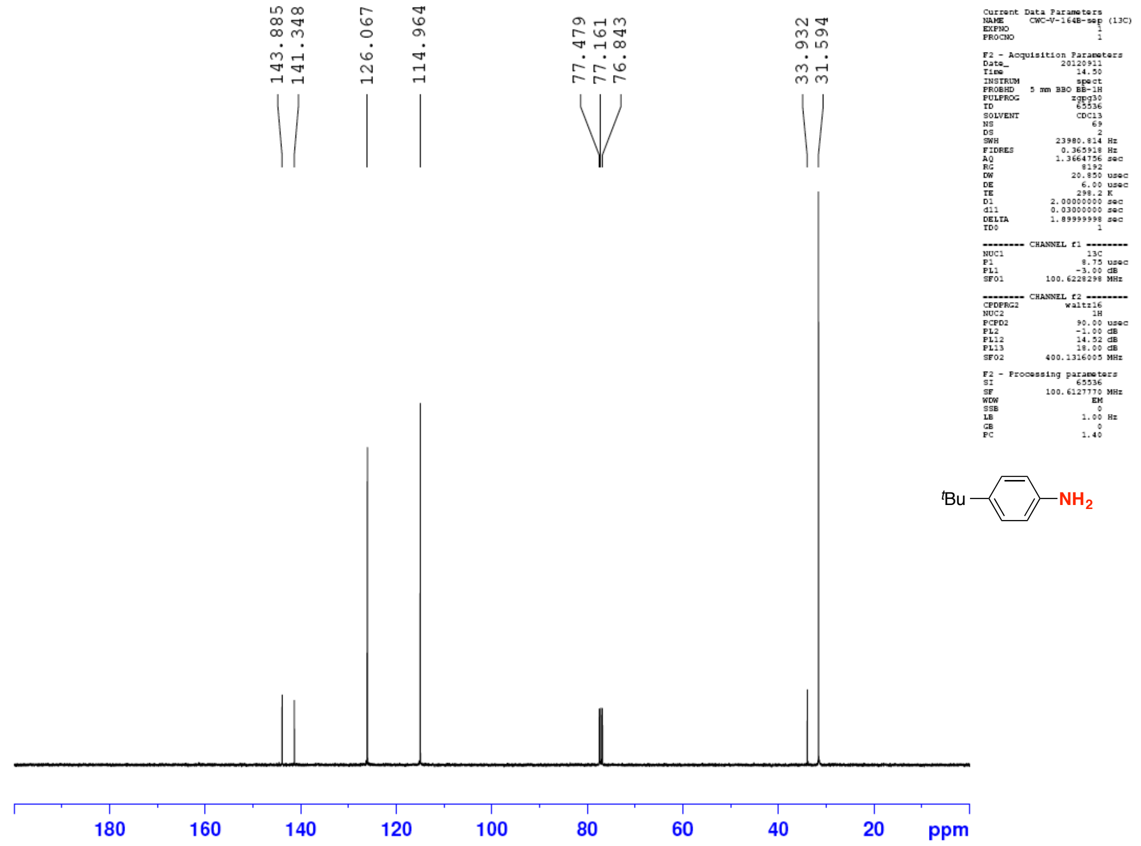
^{1}H and ^{13}C NMR of 4-(Methylthio)aniline (**4b**)



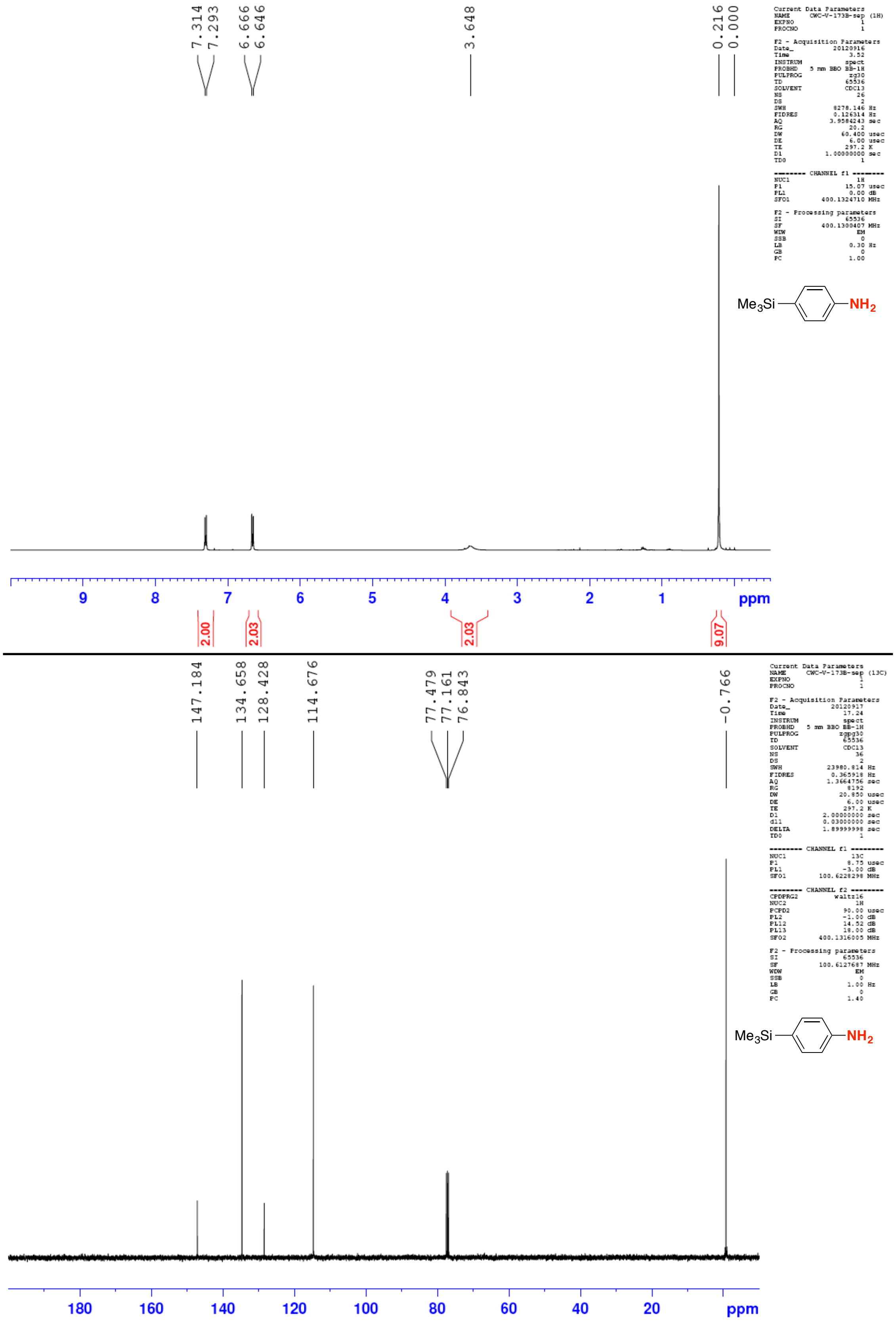


^{1}H and ^{13}C NMR of 4-(*tert*-Butyl)aniline (**4c**)





^{1}H and ^{13}C NMR of 4-(Trimethylsilyl)aniline (**4d**)



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Current Data Parameters
NAME       CWC-V-173B-sep (1H)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120916
Time                  3.52
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      26
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    20.2
DW                  60.400 usec
DE                    6.00 usec
TE                   297.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300407 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```
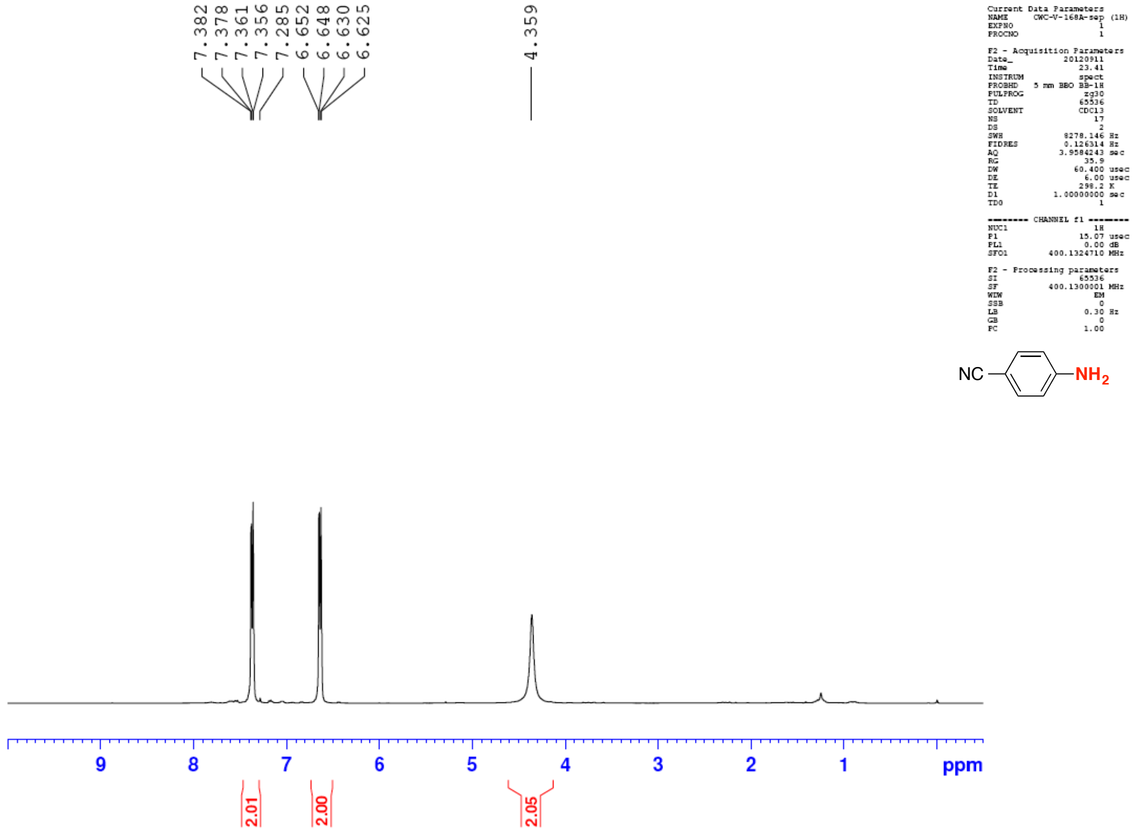
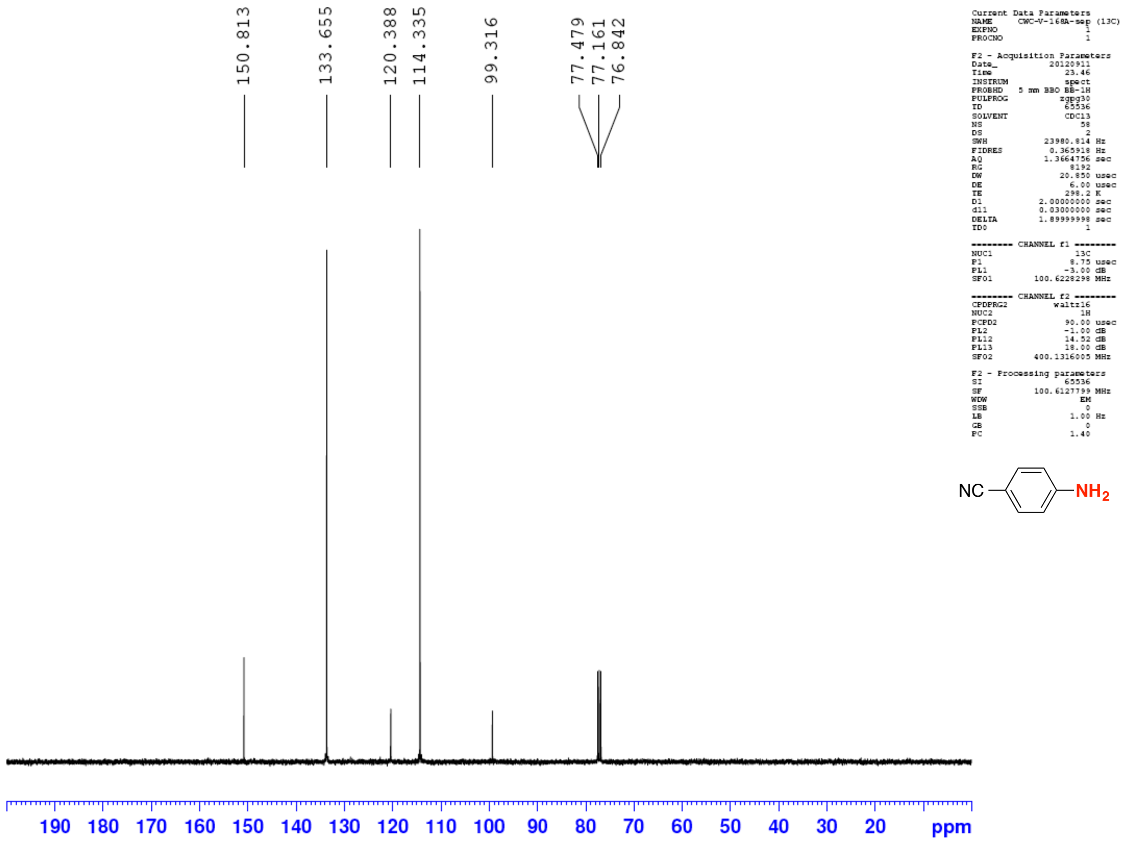

```
Current Data Parameters
NAME       CWC-V-173B-sep (13C)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120917
Time                 17.24
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                    8192
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127687 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of 4-Aminobenzonitrile (**4e**)

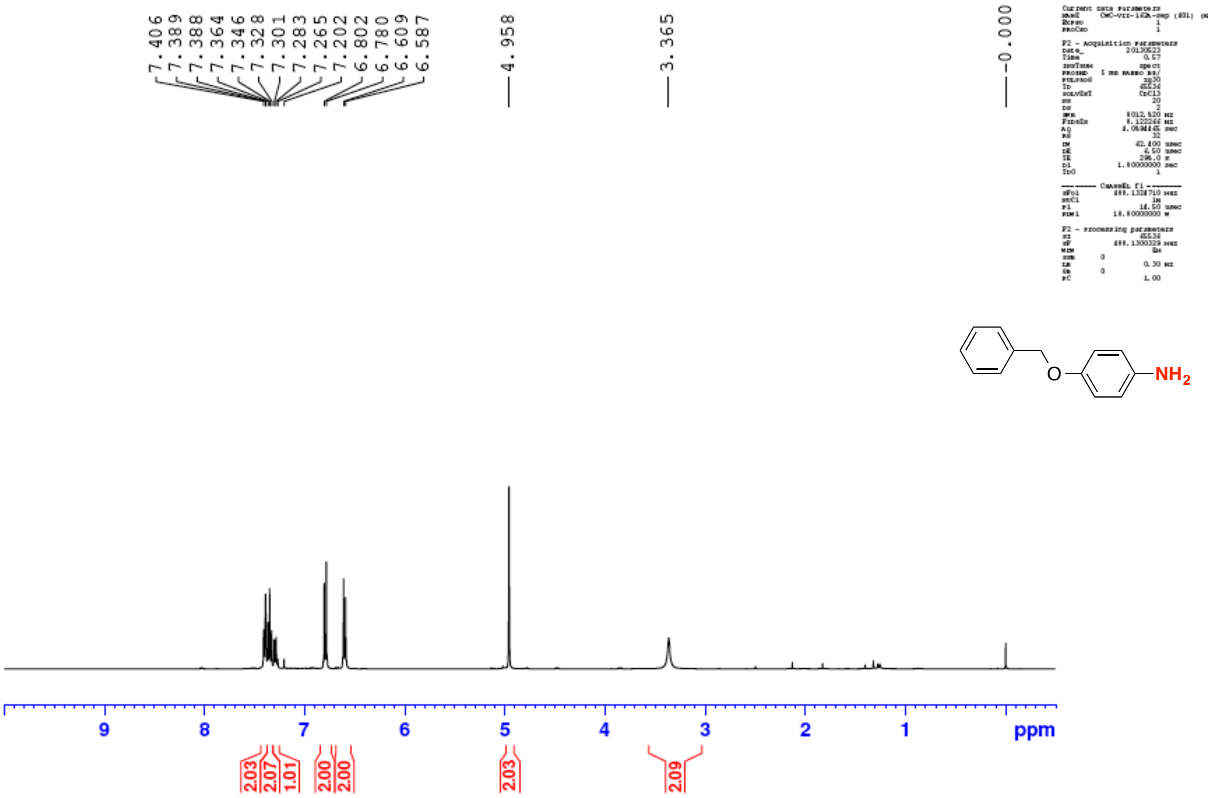


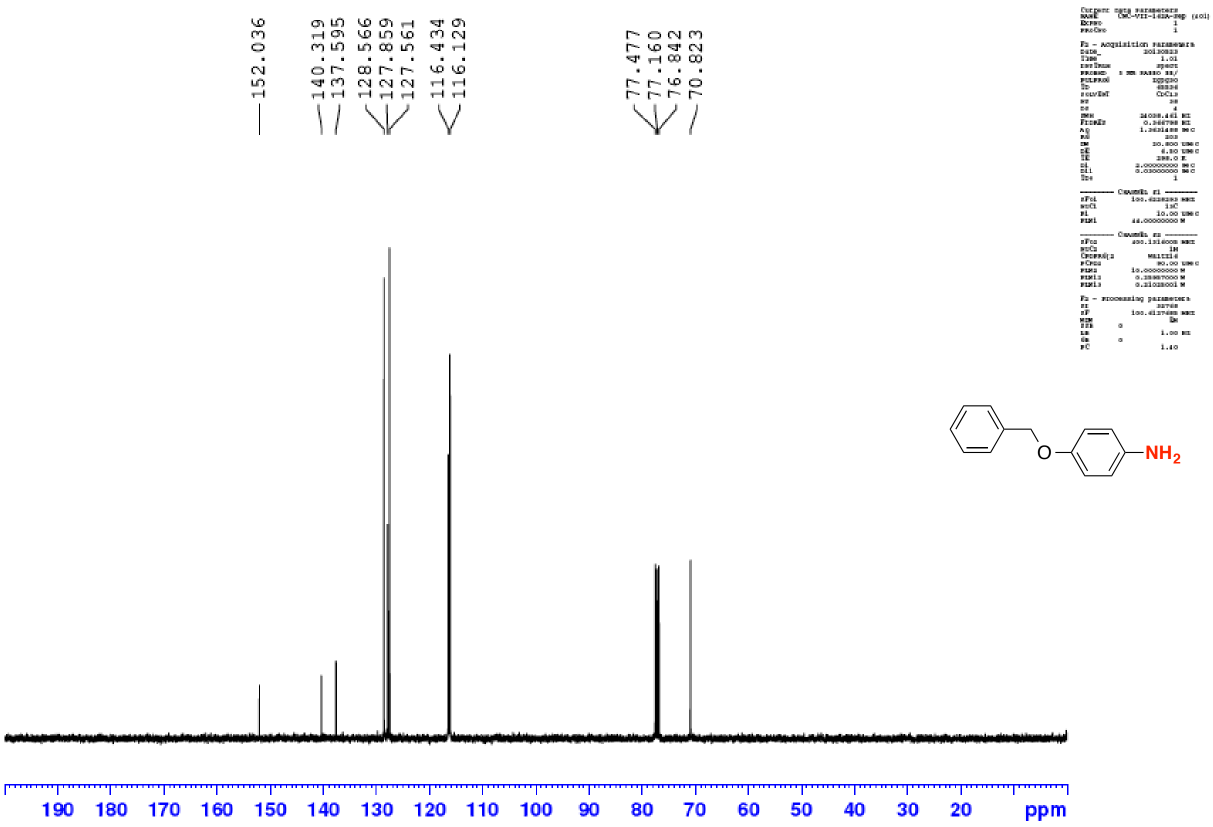
```
Current Data Parameters
NAME     CWC-V-168A-sep (1H)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120911
Time                  23.41
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       17
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                     35.9
DW                   60.400 usec
DE                     6.00 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.07 usec
PL1                    0.00 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF              400.1300001 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```



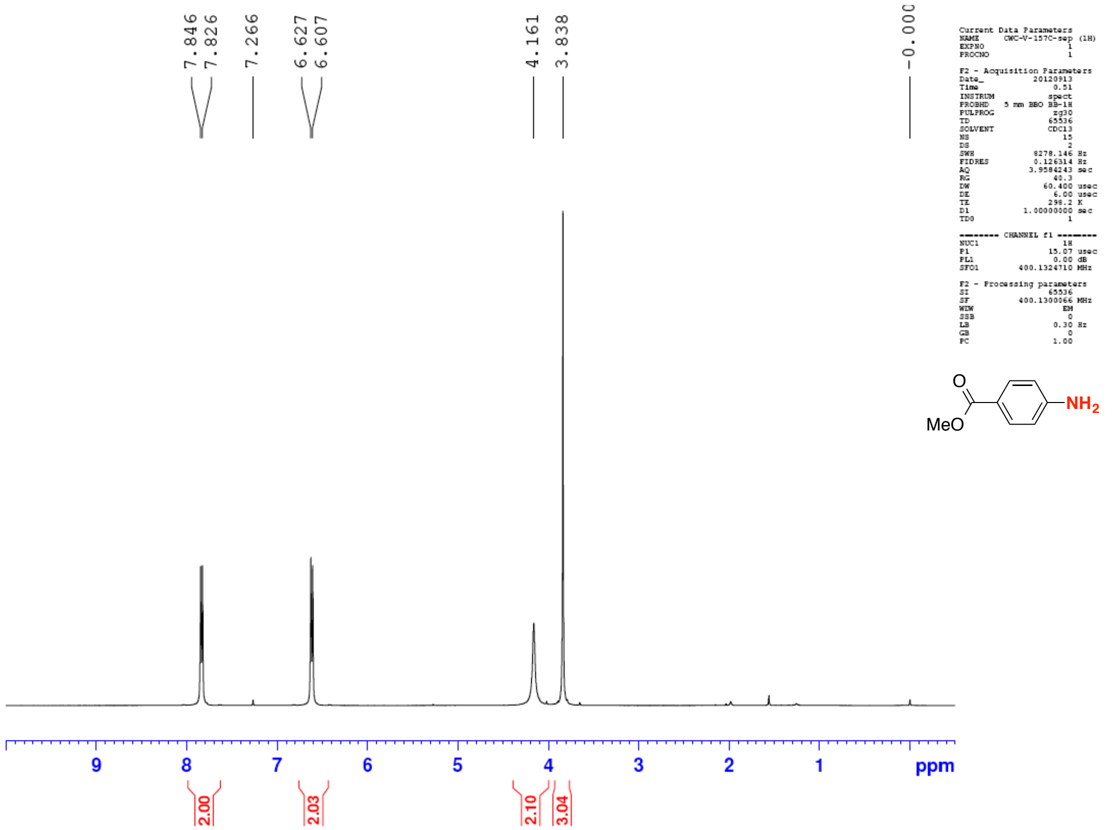
```
Current Data Parameters
NAME     CWC-V-168A-sep (13C)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120911
Time                  23.46
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       58
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                     8192
DW                   20.850 usec
DE                     6.00 usec
TE                    298.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.75 usec
PL1                   -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -1.00 dB
PL12                  14.52 dB
PL13                  18.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    65536
SF              100.6127799 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{1}H and ^{13}C NMR of 4-(Benzyloxy)aniline **(4f)**

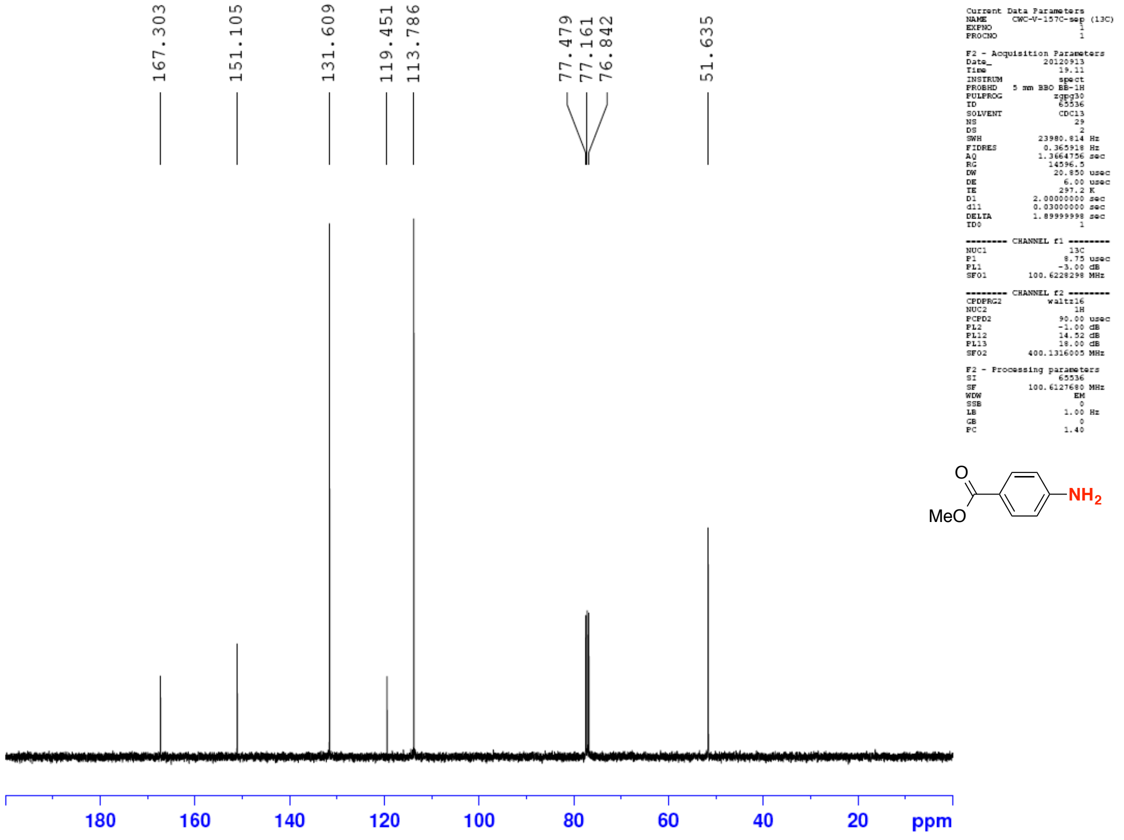




^{1}H and ^{13}C NMR of Methyl 4-Aminobenzoate (**4g**)

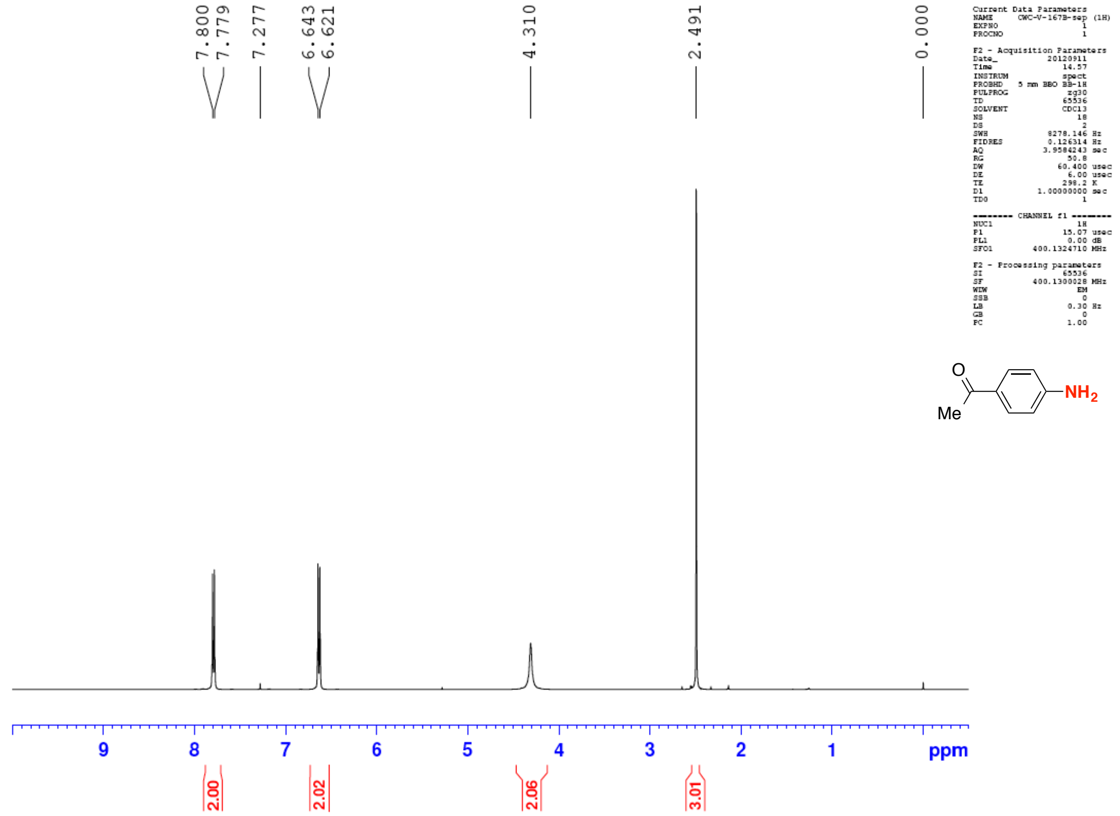


```
Current Data Parameters
NAME     CWC-V-157C-sep (1H)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120913
Time                 0.51
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     15
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   40.3
DW                 60.400 usec
DE                   6.00 usec
TE                  298.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300066 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



```
Current Data Parameters
NAME     CWC-V-157C-sep (13C)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120913
Time                19.11
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     29
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                14596.5
DW                 20.850 usec
DE                   6.00 usec
TE                  297.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127680 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^1H and ^{13}C NMR of 4’-Aminoacetophenone (**4h**)



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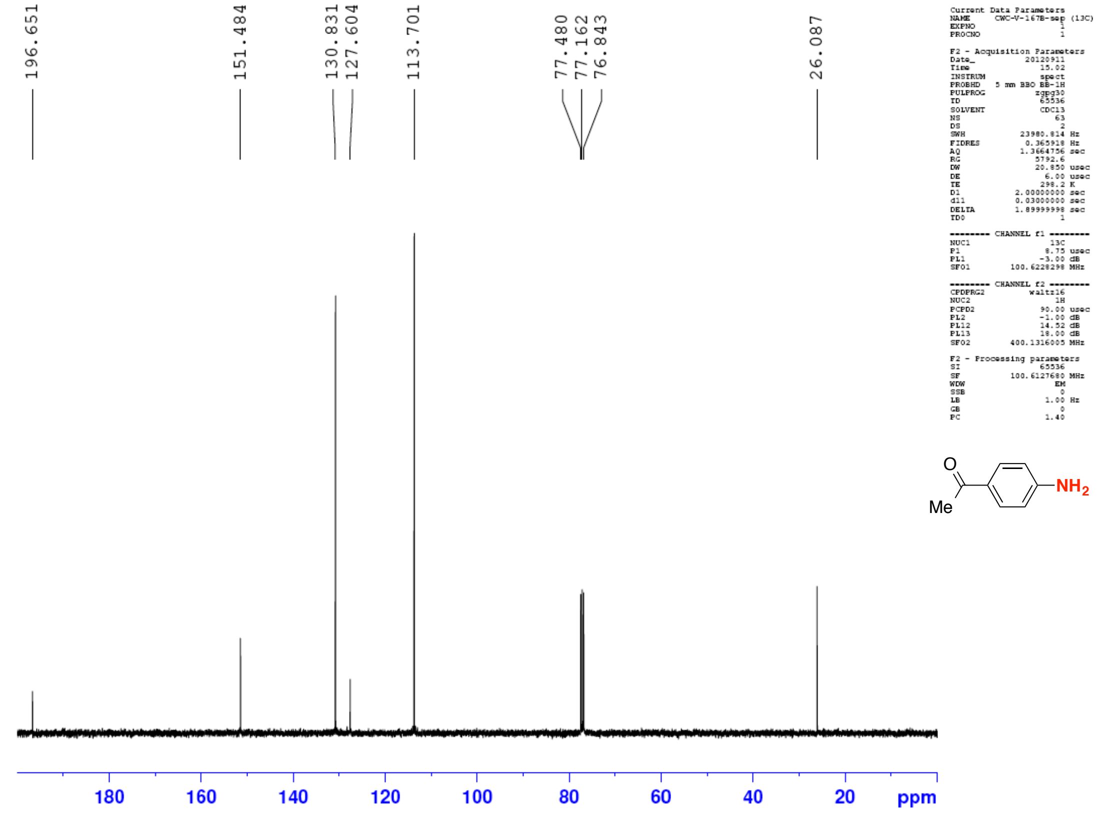
Current Data Parameters
NAME     CWC-V-167B-sep (1H)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120911
Time               14.57
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    18
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  50.8
DW                60.400 usec
DE                  6.00 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300028 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



```
Current Data Parameters
NAME     CWC-V-167B-sep (13C)
EXPNO                  1
PROCNO                 1

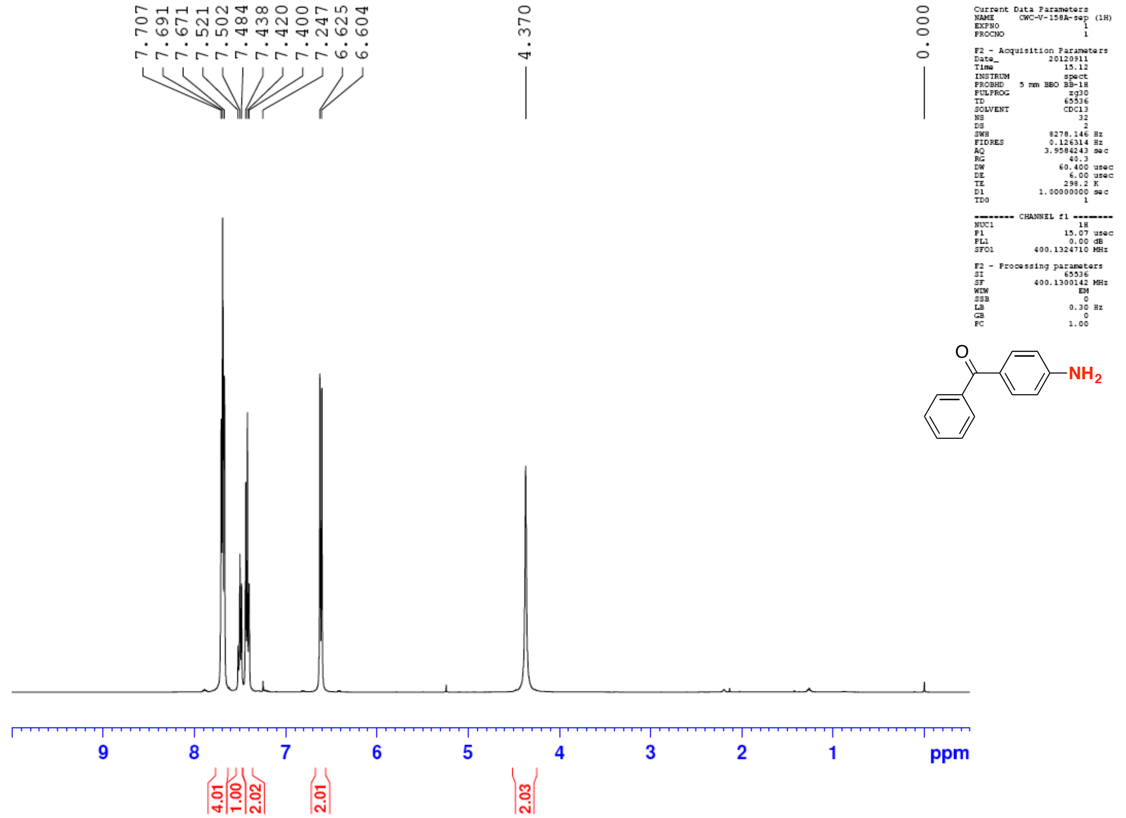
F2 - Acquisition Parameters
Date_           20120911
Time               15.02
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    63
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                5792.6
DW                20.850 usec
DE                  6.00 usec
TE                 298.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127680 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of 4-Aminobenzophenone (**4i**)

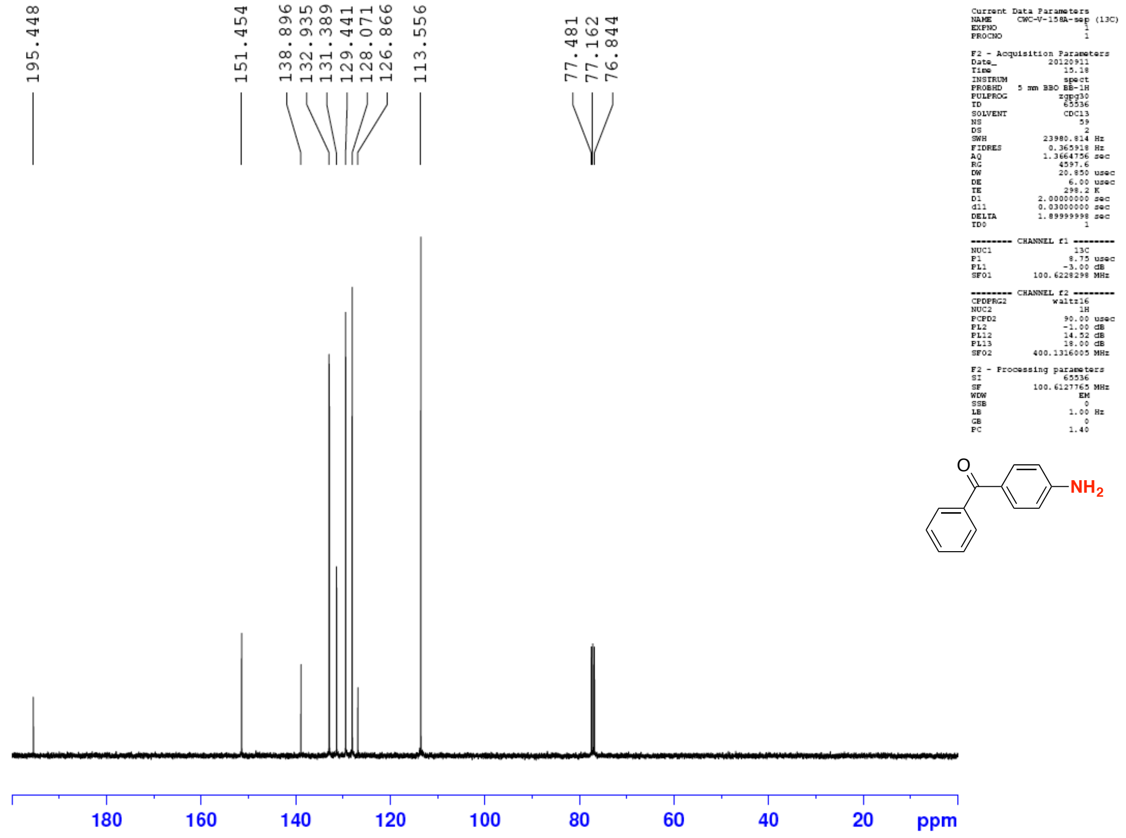


```
Current Data Parameters
NAME     CWC-V-158A-sep (1H)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120911
Time                 15.12
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    40.3
DW                  60.400 usec
DE                    6.00 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300142 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
Current Data Parameters
NAME     CWC-V-158A-sep (13C)
EXPNO                    1
PROCNO                   1

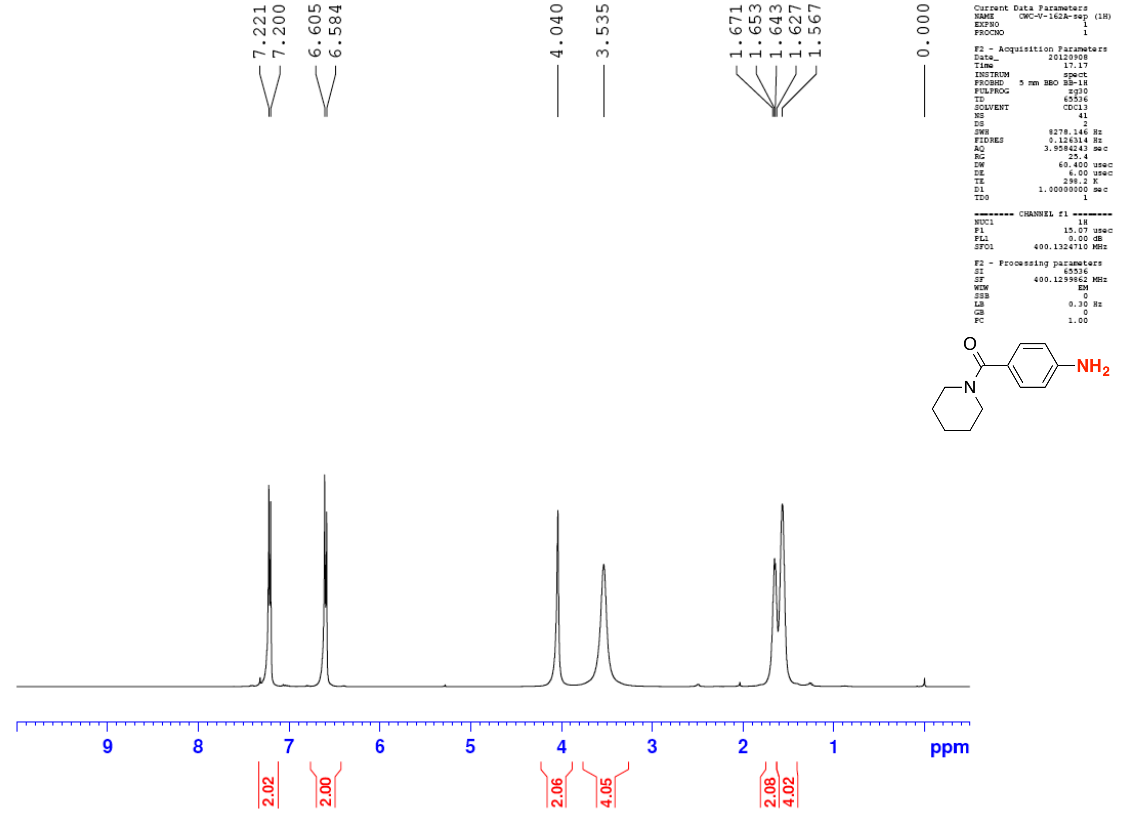
F2 - Acquisition Parameters
Date_             20120911
Time                 15.18
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      59
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  4597.6
DW                  20.850 usec
DE                    6.00 usec
TE                   298.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127765 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of (4-Aminophenyl)(piperidin-1-yl)methanone (**4j**)

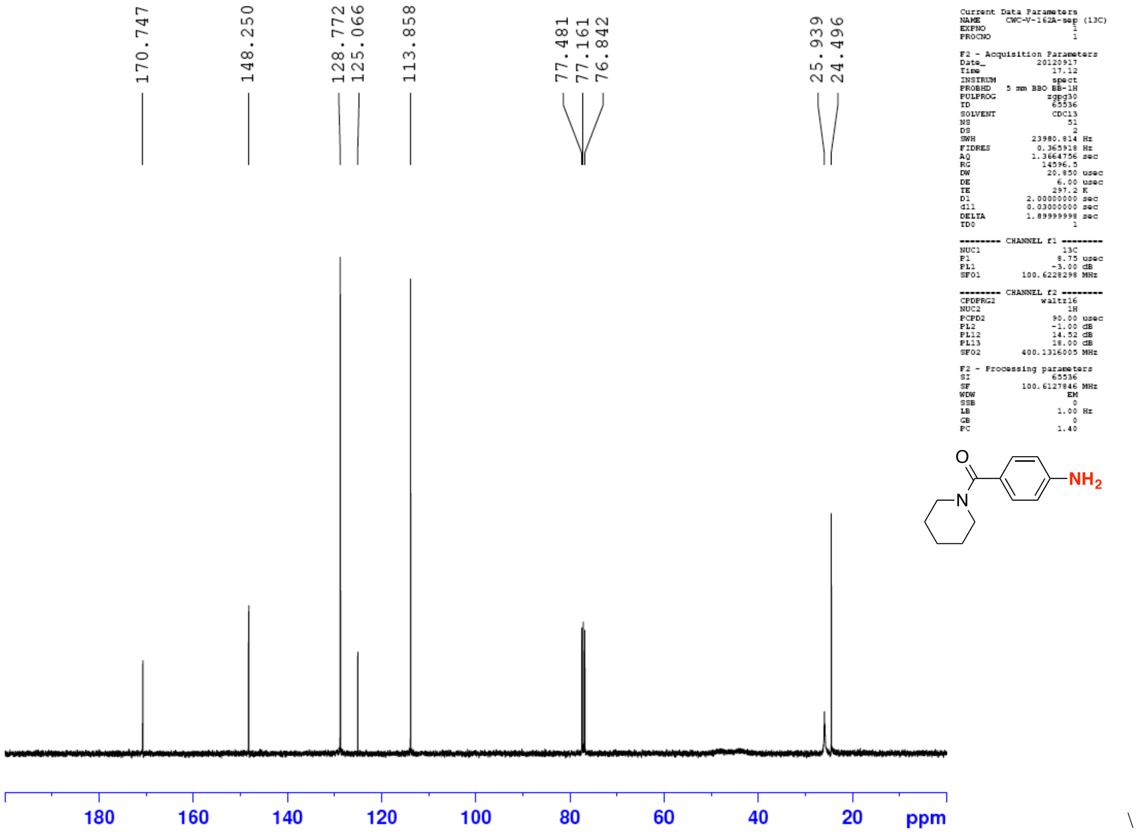


```
Current Data Parameters
NAME      CWC-V-162A-sep (1H)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120908
Time                 17.17
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      41
DS                       2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                    25.4
DW                  60.400 usec
DE                    6.00 usec
TE                   298.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF           400.1299862 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



```
Current Data Parameters
NAME      CWC-V-162A-sep (13C)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120917
Time                 17.12
INSTRUM              spect
PROBHD    5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      51
DS                       2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                 14596.5
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF           100.6127846 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

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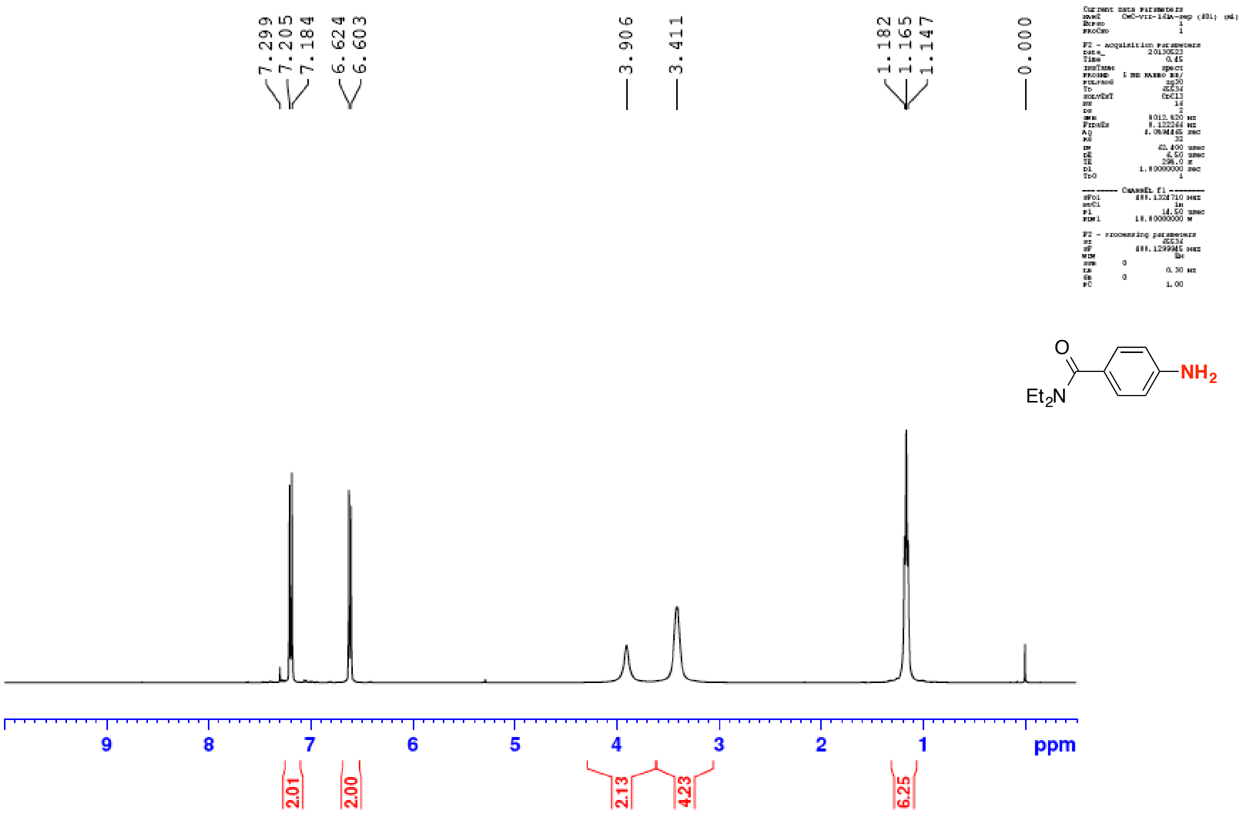
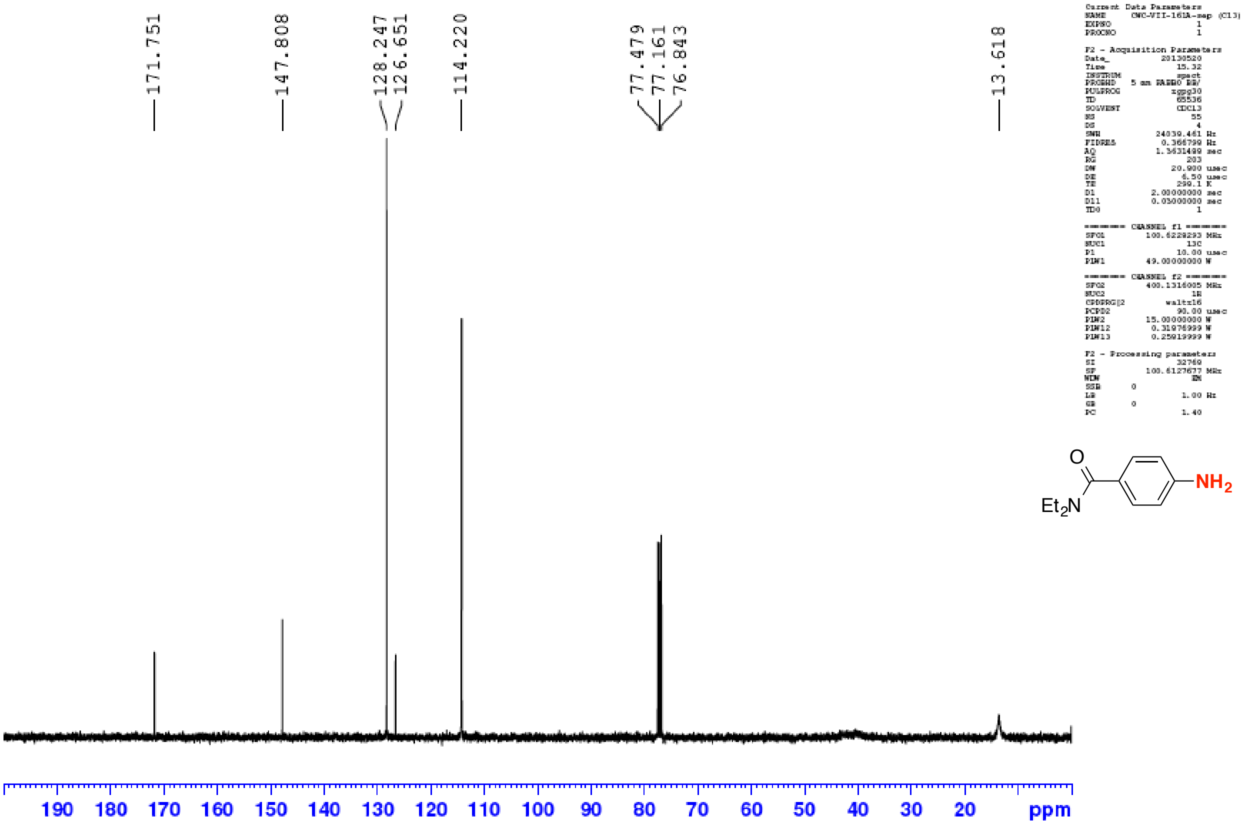
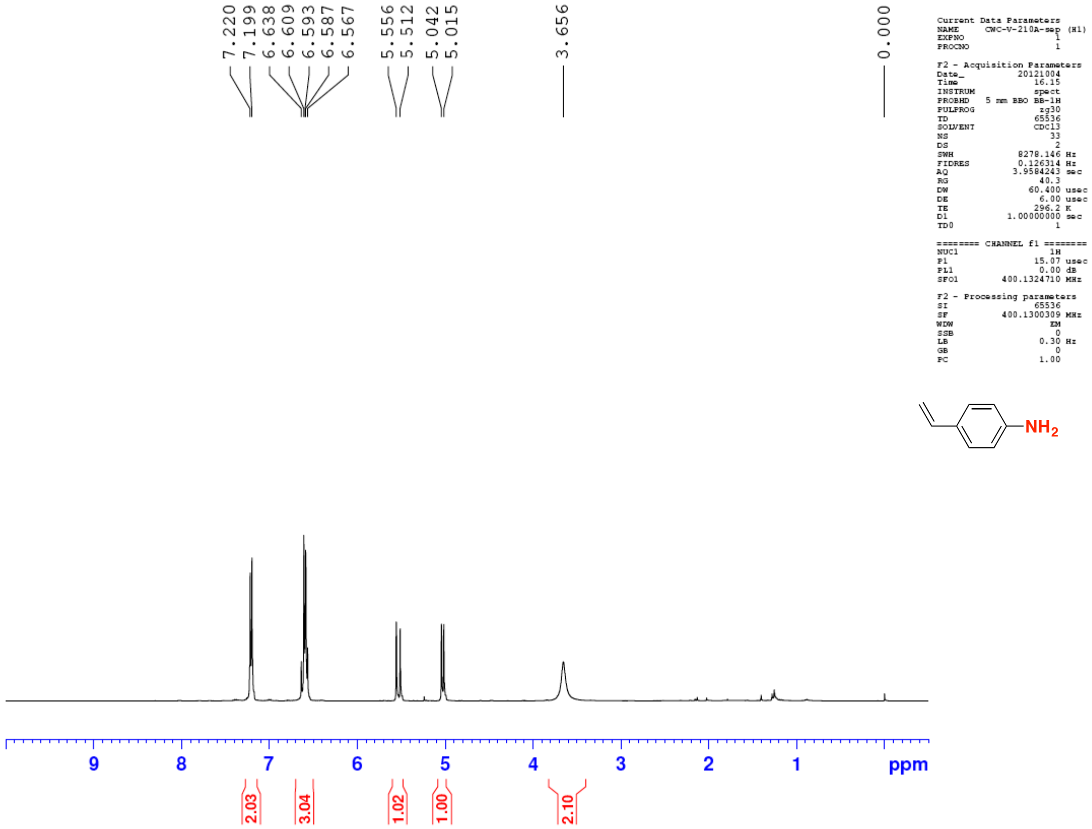
^{1}H and ^{13}C NMR of 4-Amino-*N*,*N*-diethylbenzamide **(4k)**





^{1}H and ^{13}C NMR of 4-Vinylaniline (**4l**)



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Current Data Parameters
NAME     CWC-V-210A-sep (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121004
Time                 16.15
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      33
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    40.3
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300309 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```
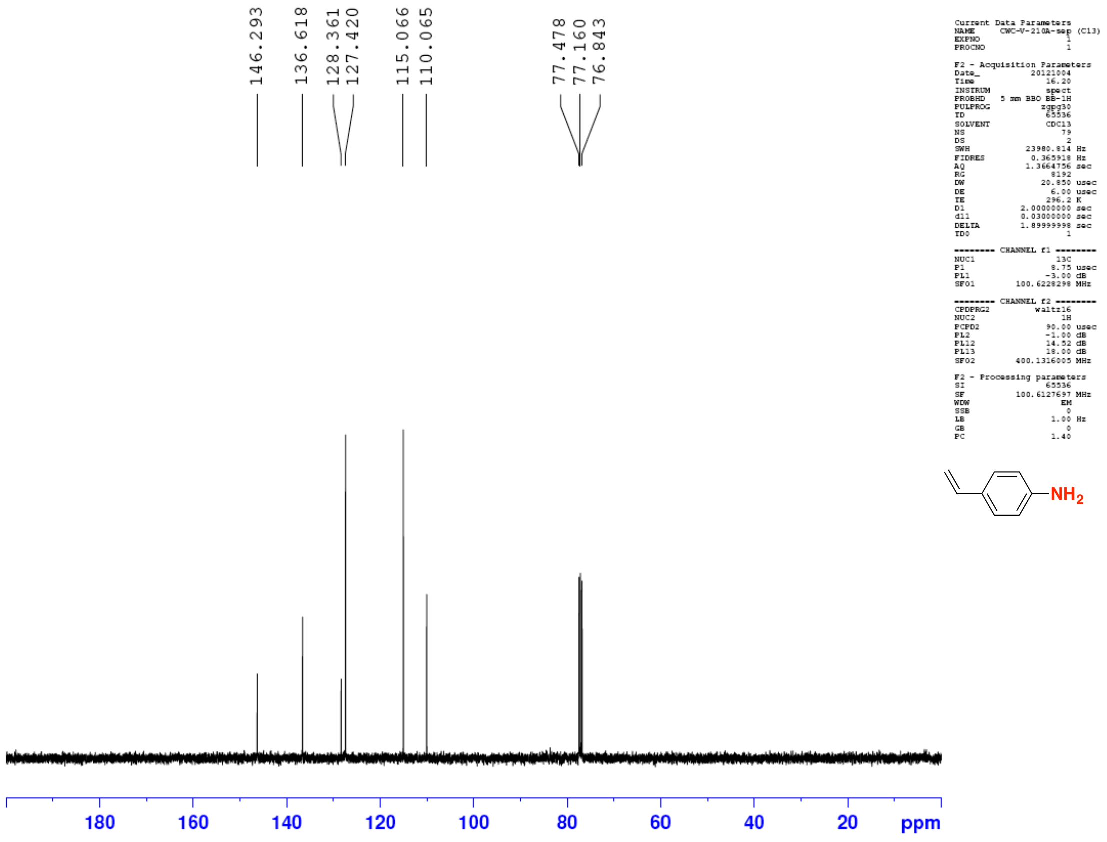
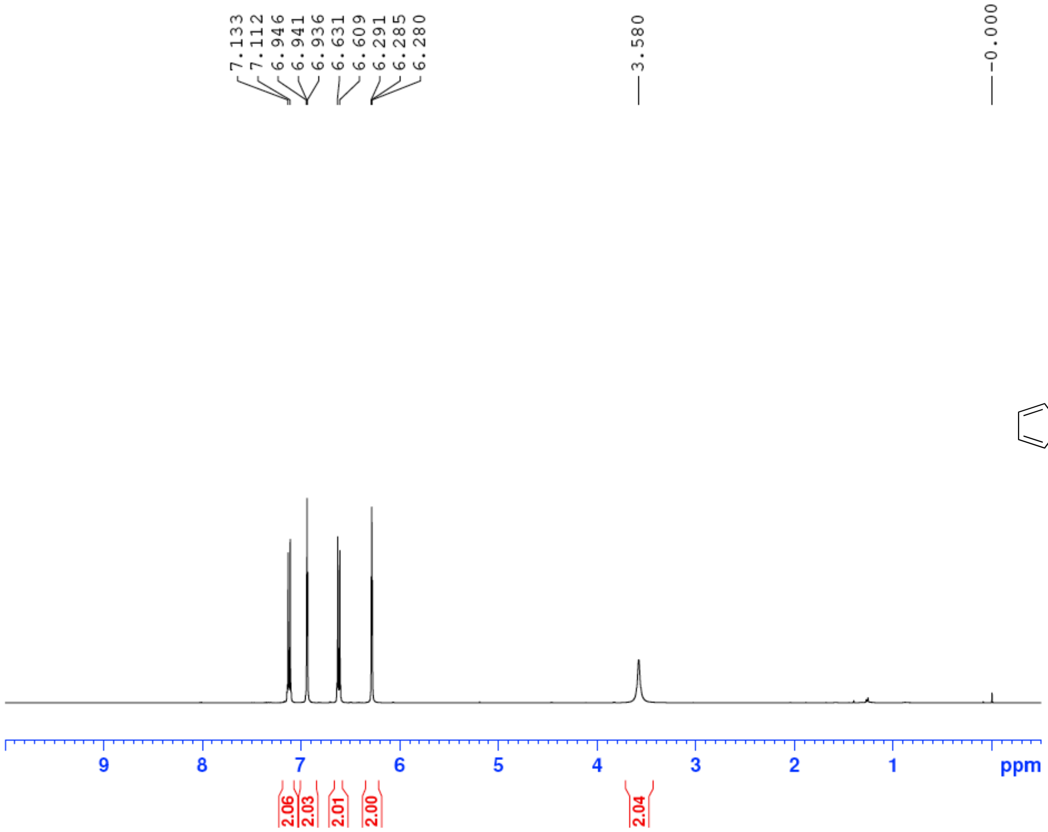
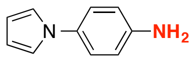



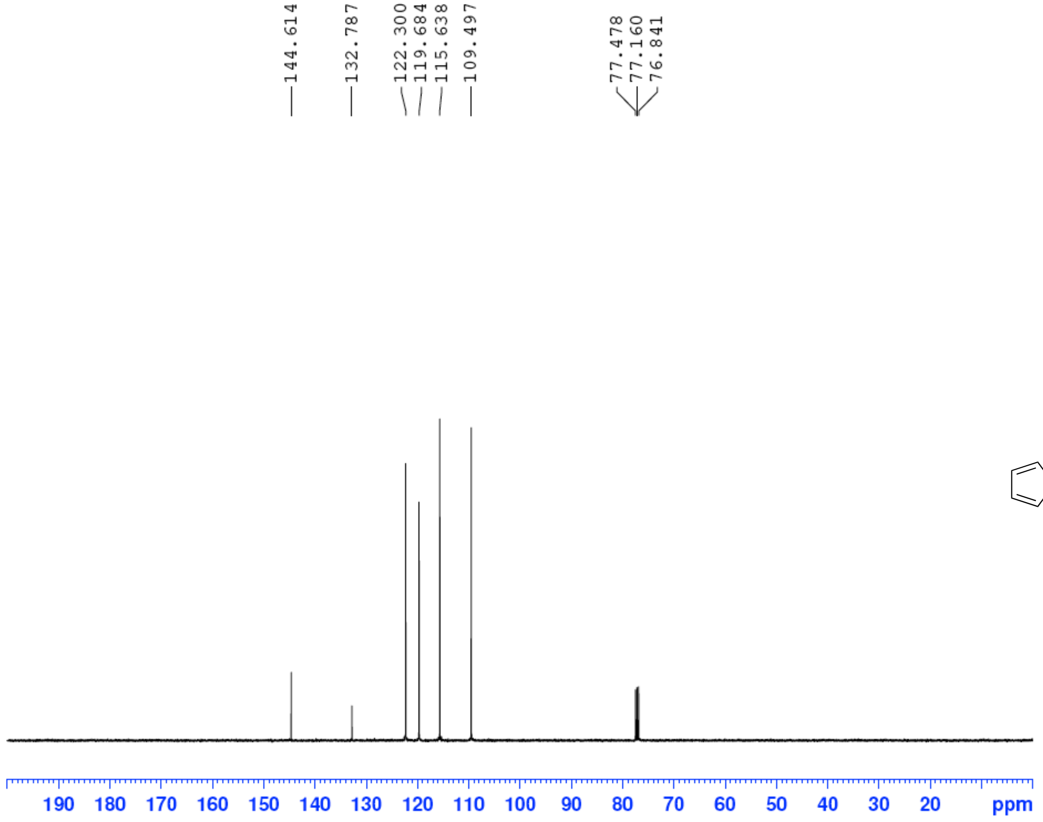
```
Current Data Parameters
NAME     CWC-V-210A-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121004
Time                 16.20
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      79
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                    8192
DW                  20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127697 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of 4-(1*H*-Pyrrol-1-yl)aniline (**4m**)

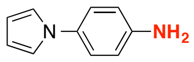


```
Current Data Parameters
NAME     CWC-VI-64B-sep (H1)
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20121203
Time               0.27
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   37
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                   32
DW               62.400 usec
DE                 6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                14.50 usec
PLW1        10.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1300554 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

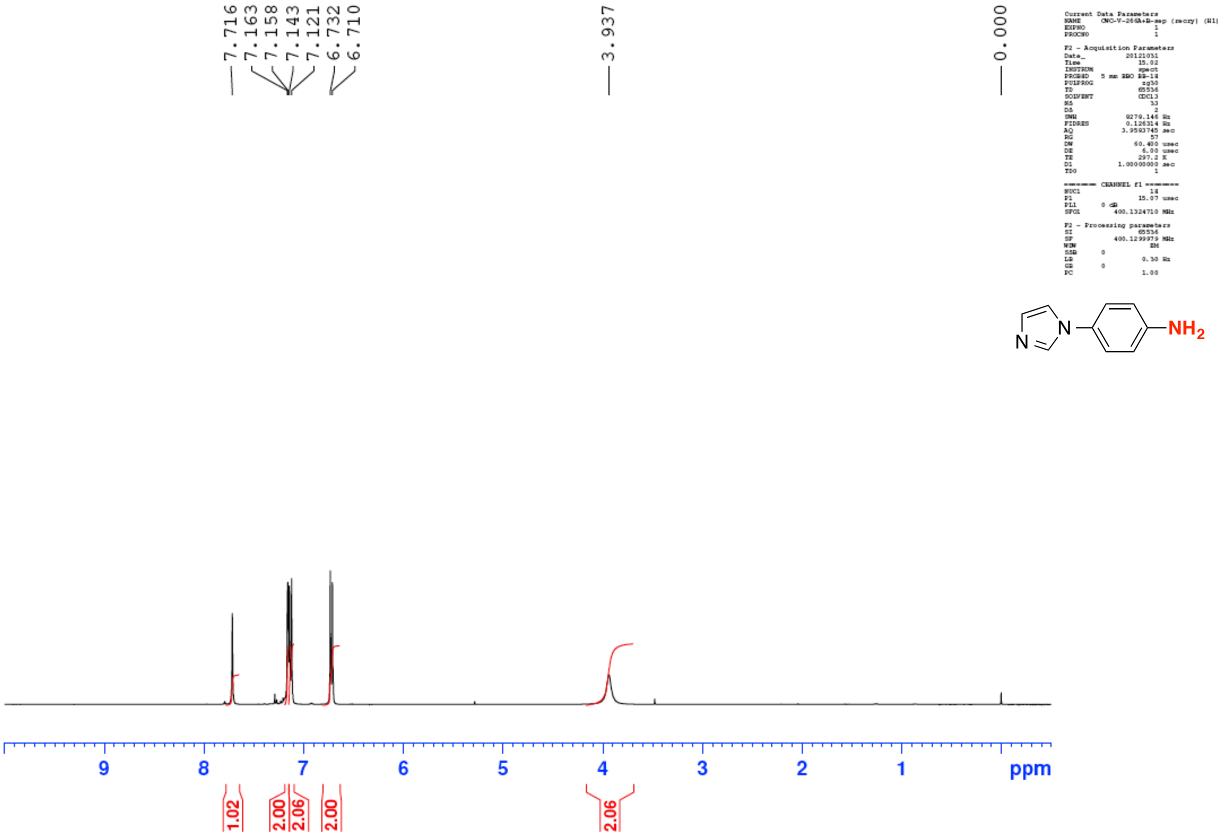


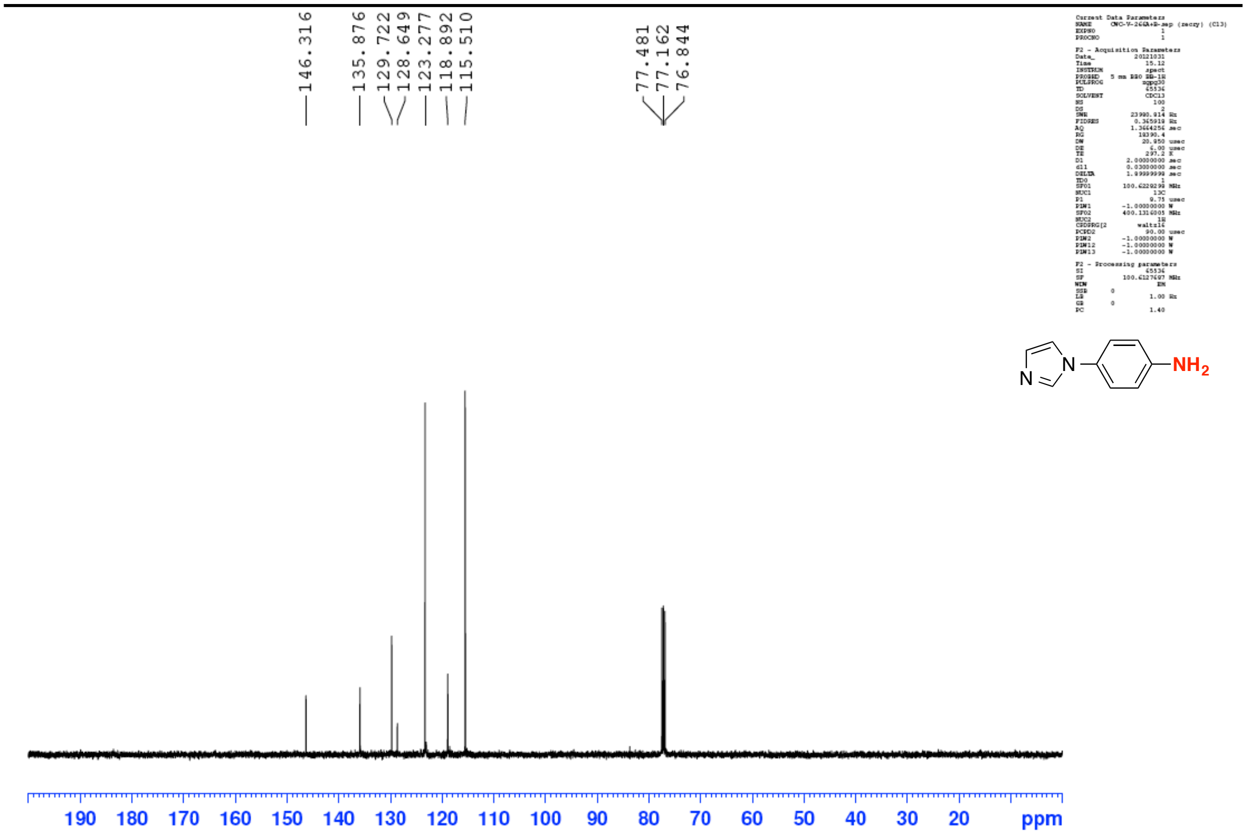


```
Current Data Parameters
NAME     CWC-VI-64B-sep (C13)
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20121203
Time               0.30
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   44
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        44.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        10.00000000 W
PLW12        0.25957000 W
PLW13        0.21025001 W

F2 - Processing parameters
SI                32768
SF          100.6127803 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

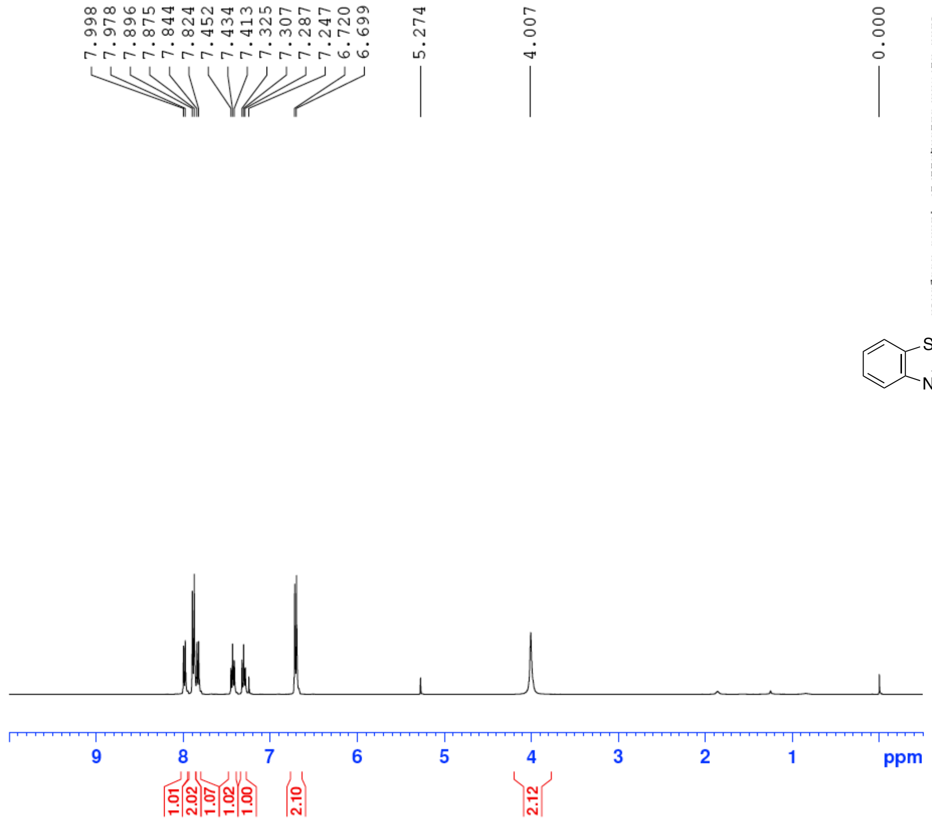


^{1}H and ^{13}C NMR of 4-(1*H*-Imidazol-1-yl)aniline (**4n**)

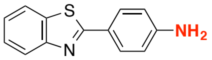


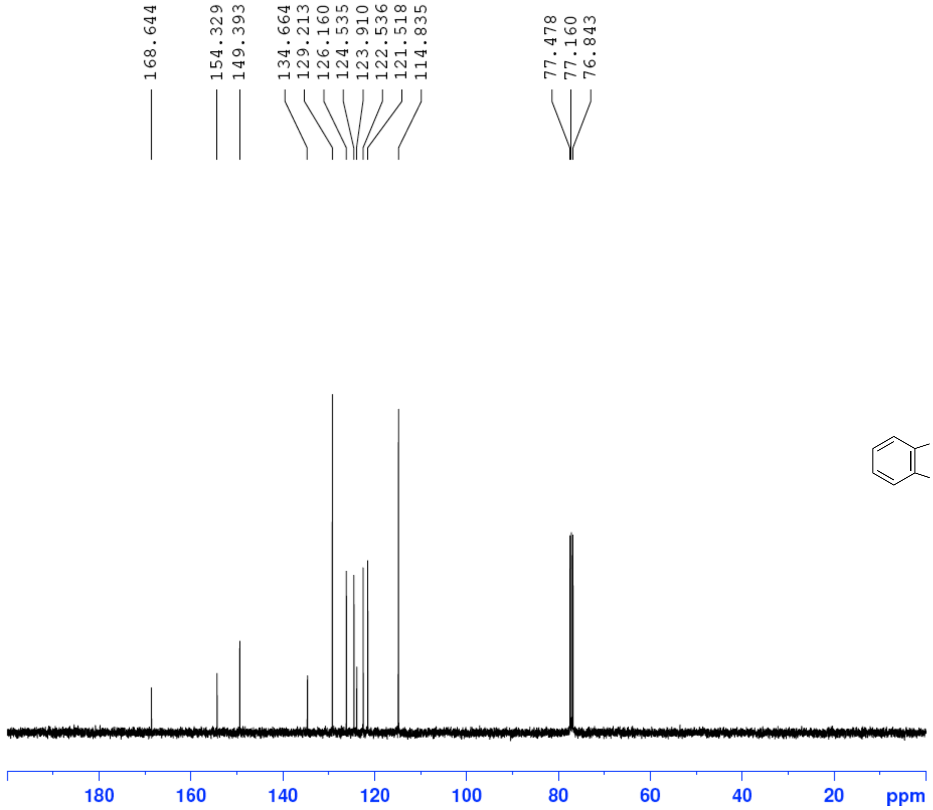


^{1}H and ^{13}C NMR of 4-(Benzothiazol-2-yl)aniline (**4o**)

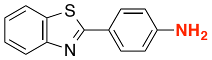


```
Current Data Parameters
NAME       CWC-V-227B-sep (2) (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121023
Time                 13.54
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      21
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                     128
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1              3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300152 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

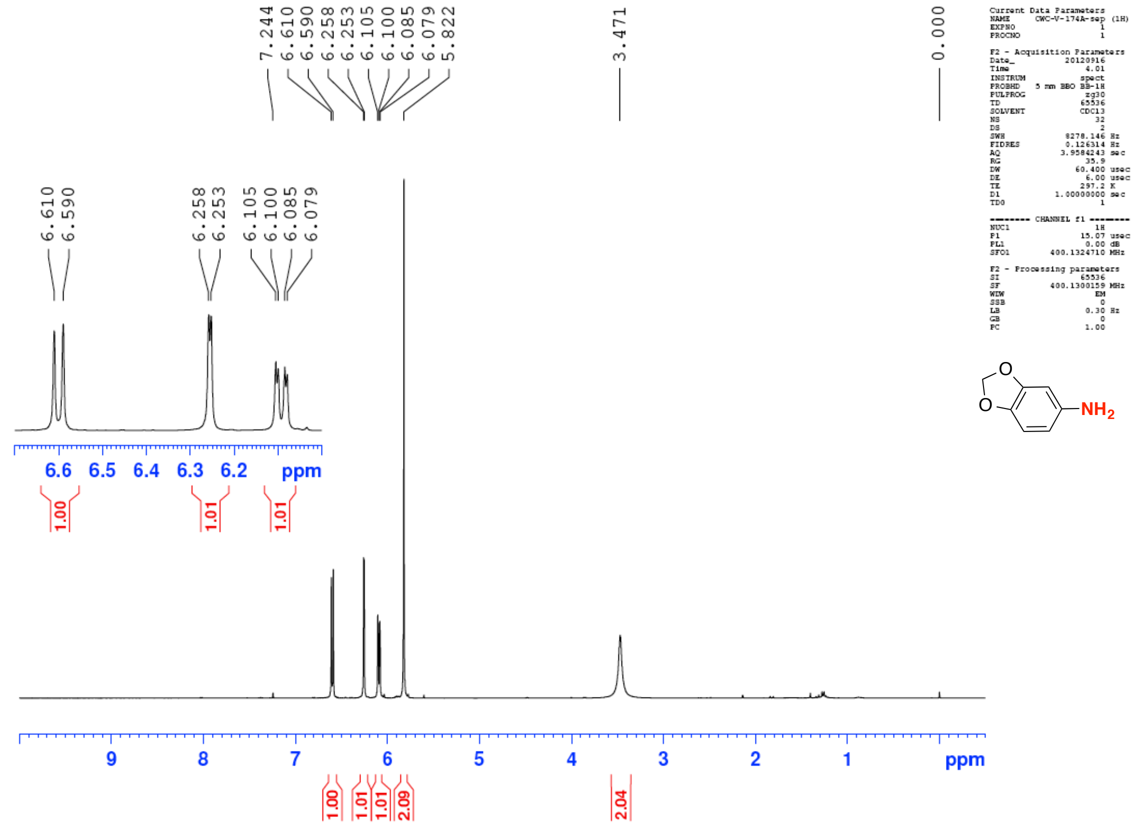




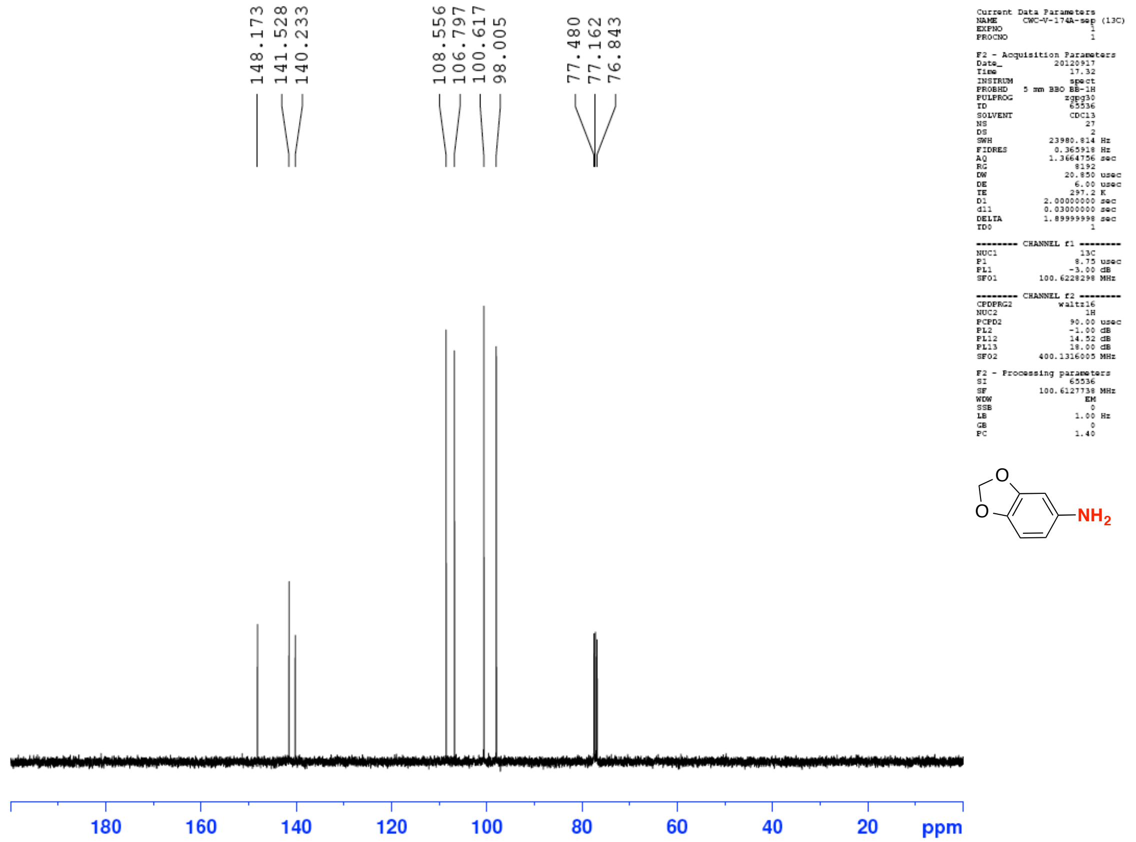
```
Current Data Parameters
NAME       CWC-V-227B-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121019
Time                 20.50
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      78
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                  5792.6
DW                  20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127643 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



^{1}H and ^{13}C NMR of 5-Aminobenzo[1,3]dioxole (**4p**)

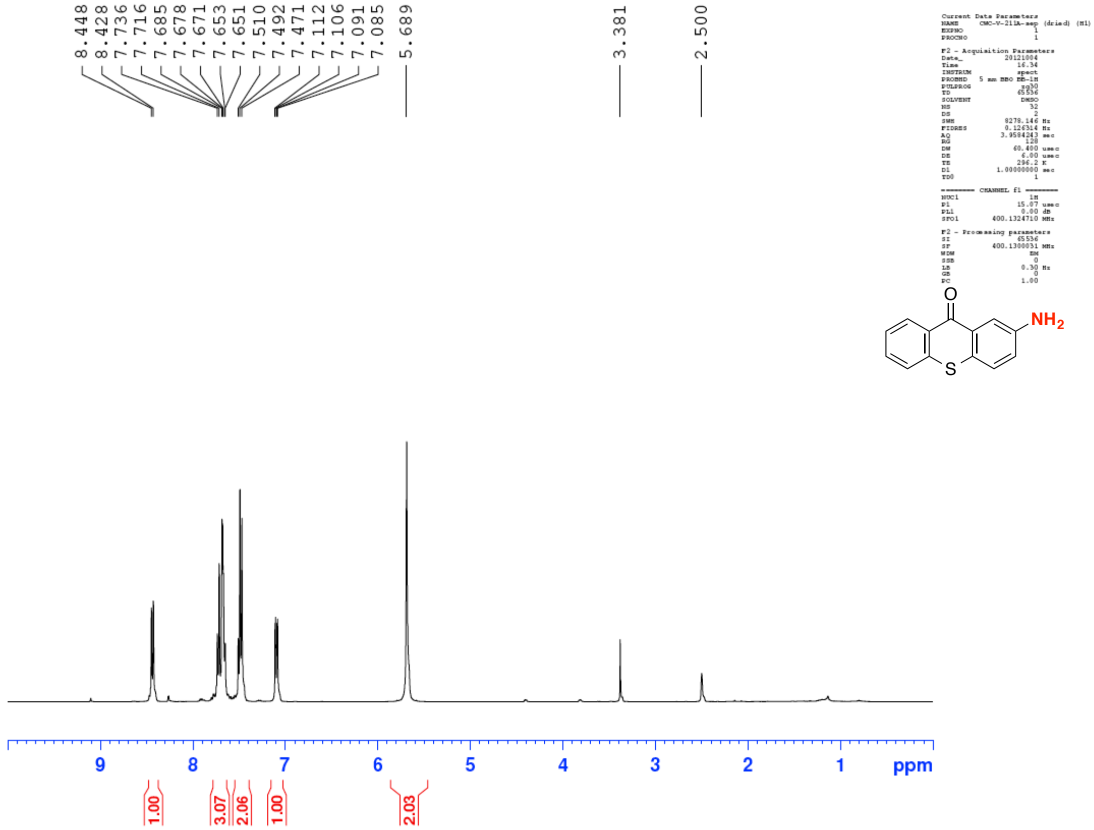


```
Current Data Parameters
NAME     CWC-V-174A-sep (1H)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120916
Time                4.01
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  35.9
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300159 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

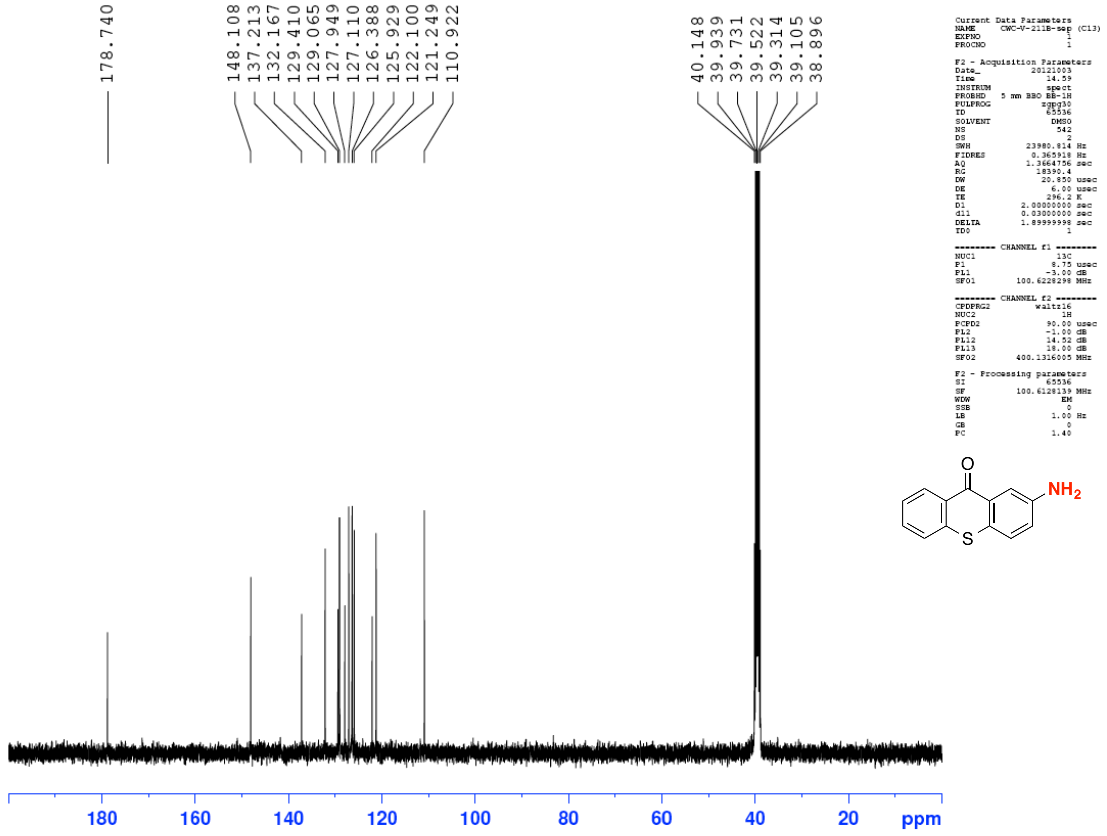


```
Current Data Parameters
NAME     CWC-V-174A-sep (13C)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120917
Time               17.32
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    27
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  8192
DW                20.850 usec
DE                  6.00 usec
TE                 297.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127738 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of 2-Amino-9*H*-thioxanthen-9-one (**4q**)

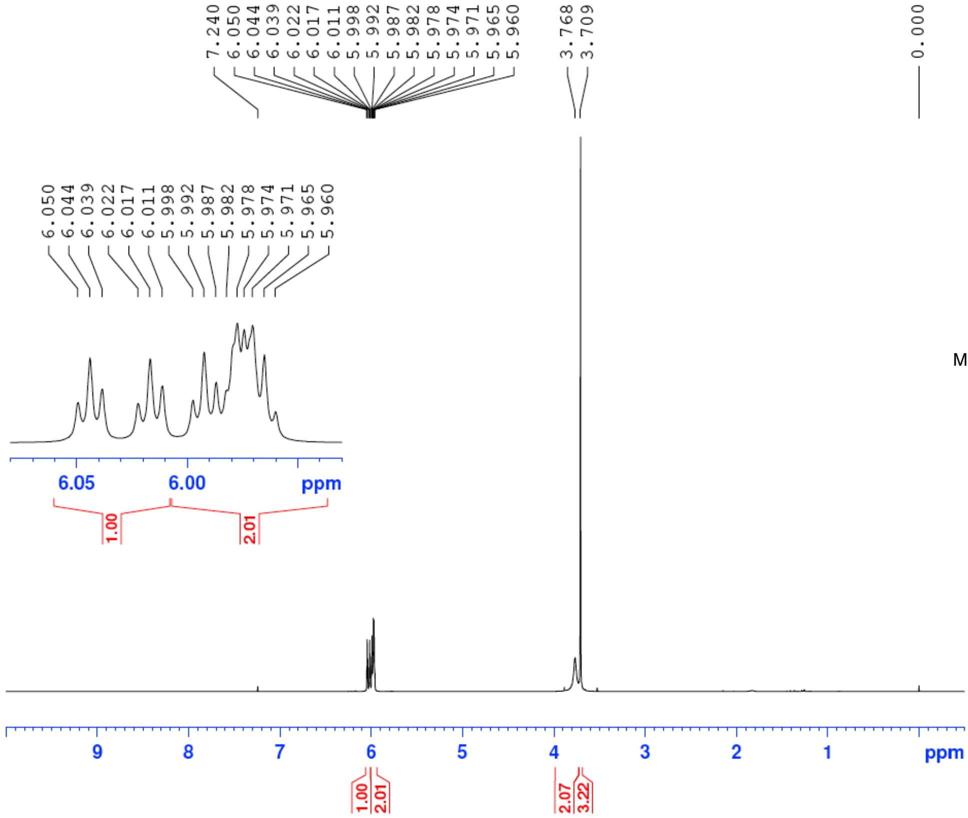


```
Current Data Parameters
NAME      CWC-V-211A-sep (dried) (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121004
Time                 16.34
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      32
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                     128
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300031 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

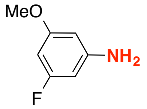


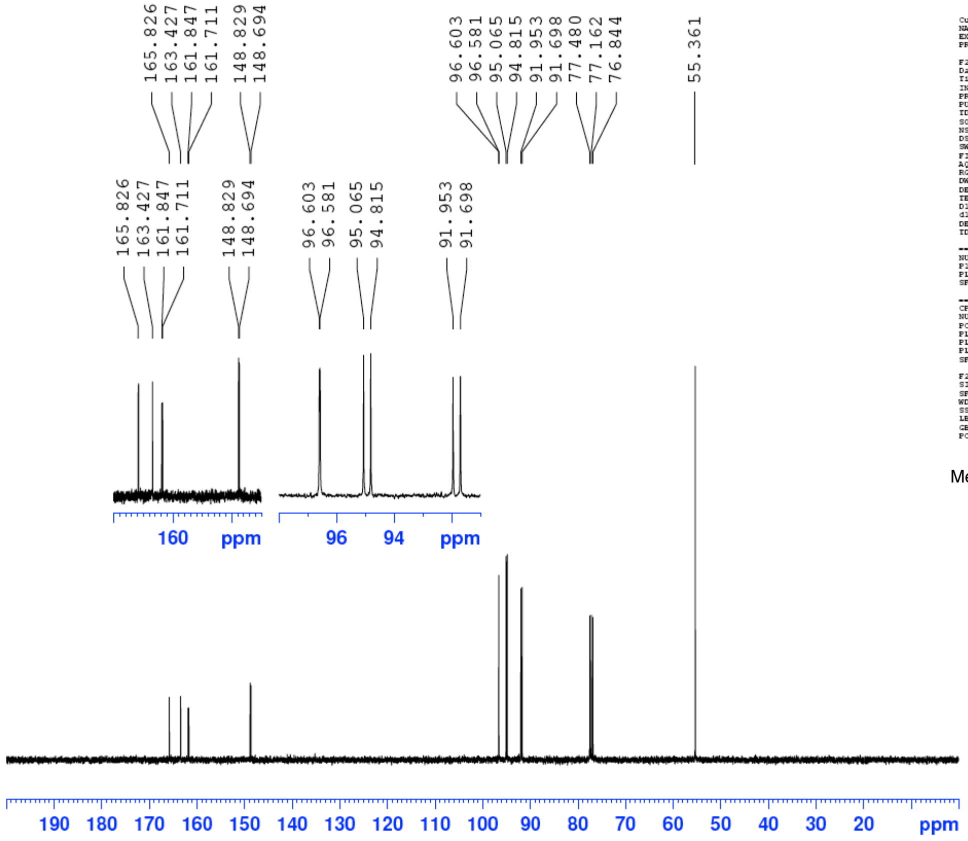
```
Current Data Parameters
NAME      CWC-V-211B-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121003
Time                 14.59
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT               DMSO
NS                     542
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6128139 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of 3-Fluoro-5-methoxyaniline (**4r**)

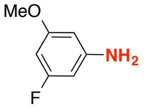


```
Current Data Parameters
NAME     CWC-V-169A-sep (1H)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120914
Time               15.19
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    24
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  35.9
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300174 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

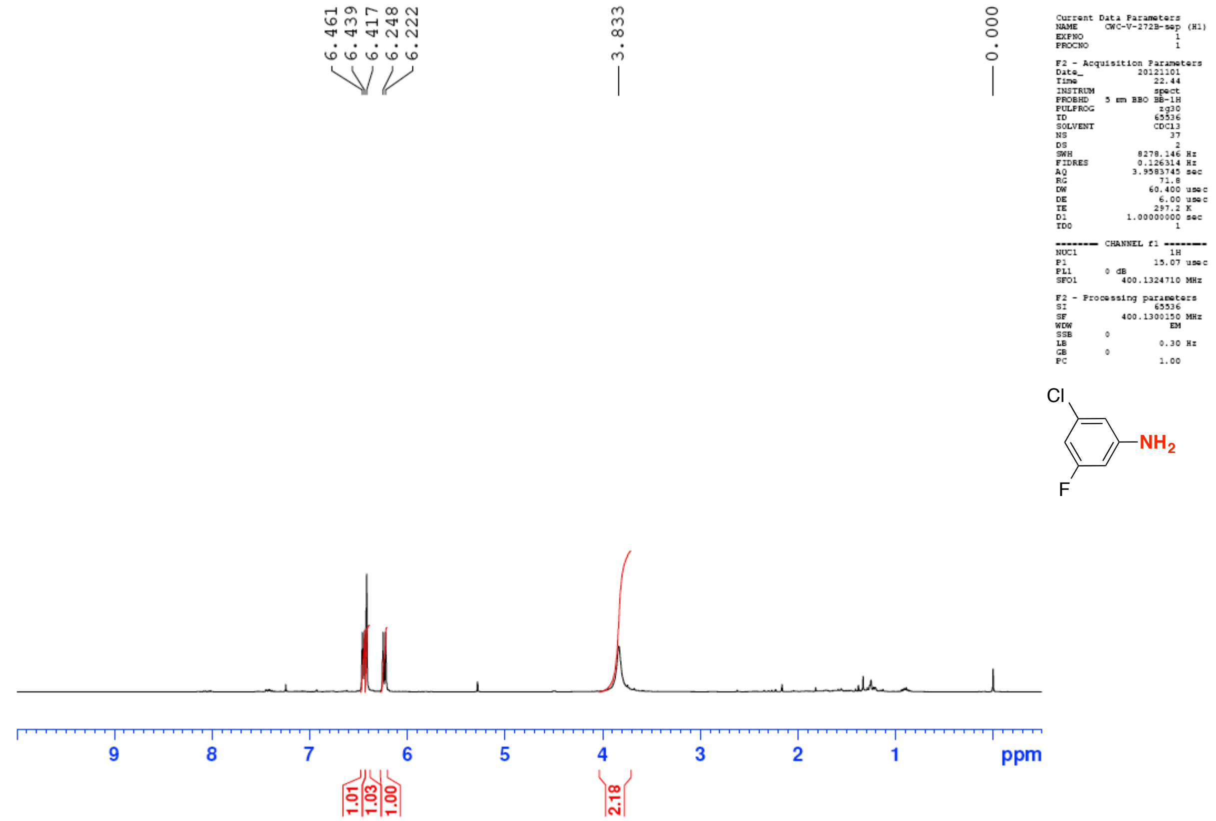




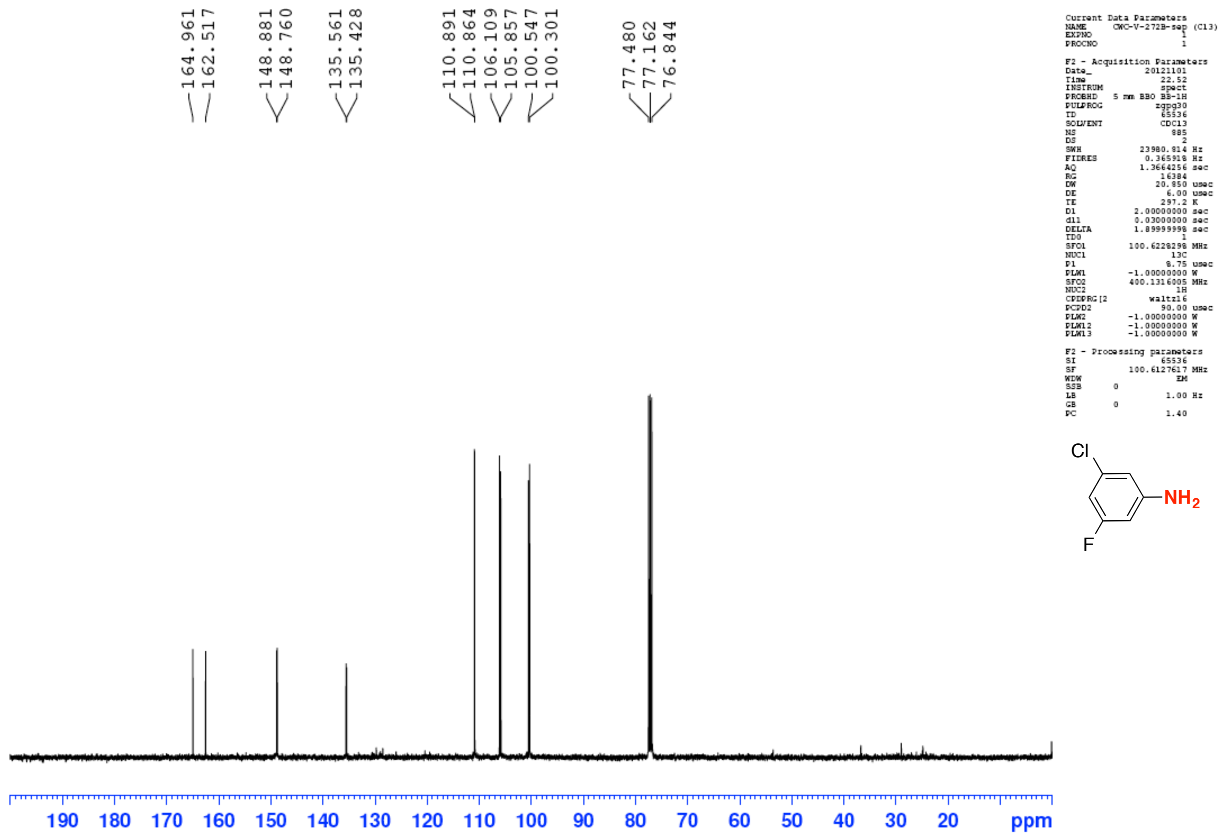
```
Current Data Parameters
NAME     CWC-V-169B-sep (13C)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120911
Time               23.35
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    68
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               14596.5
DW                20.850 usec
DE                  6.00 usec
TE                 298.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127655 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



^{1}H and ^{13}C NMR of 3-Chloro-5-fluoroaniline (**4s**)

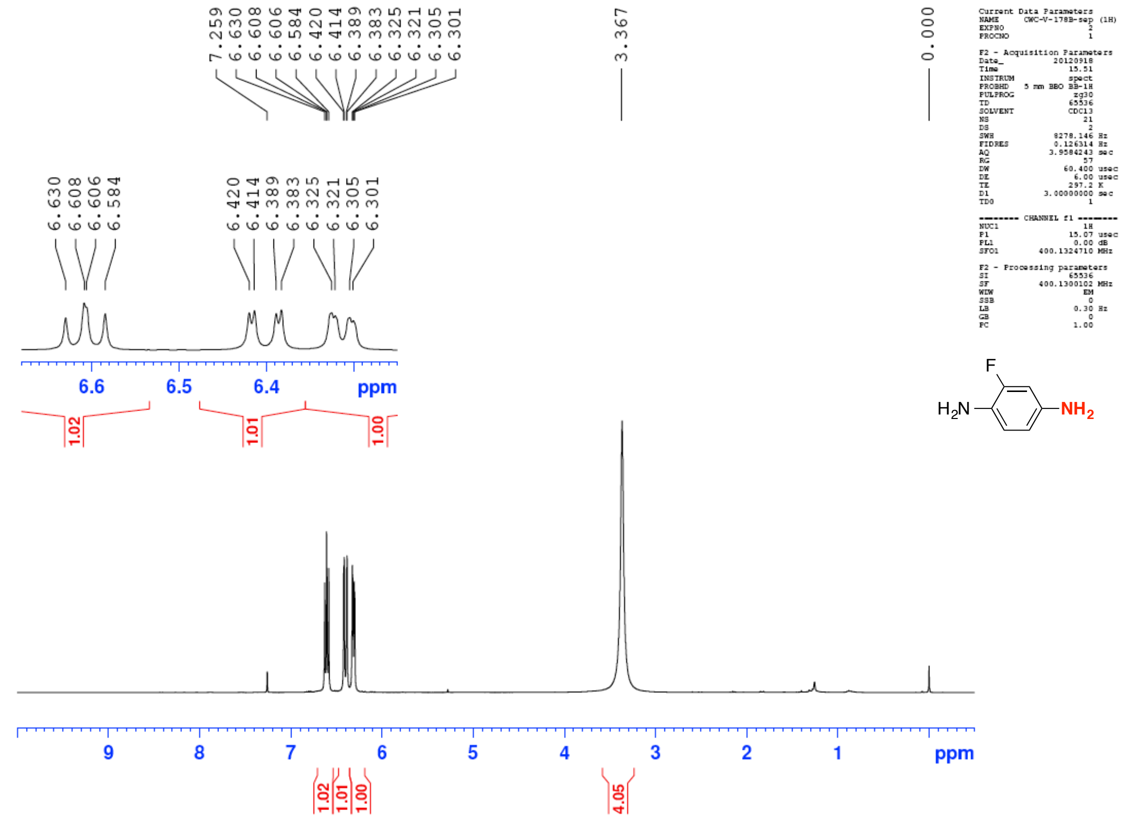


```
Current Data Parameters
NAME      CWC-V-272B-sep (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121101
Time               22.44
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                    37
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9583745 sec
RG                  71.8
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1      0 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300150 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

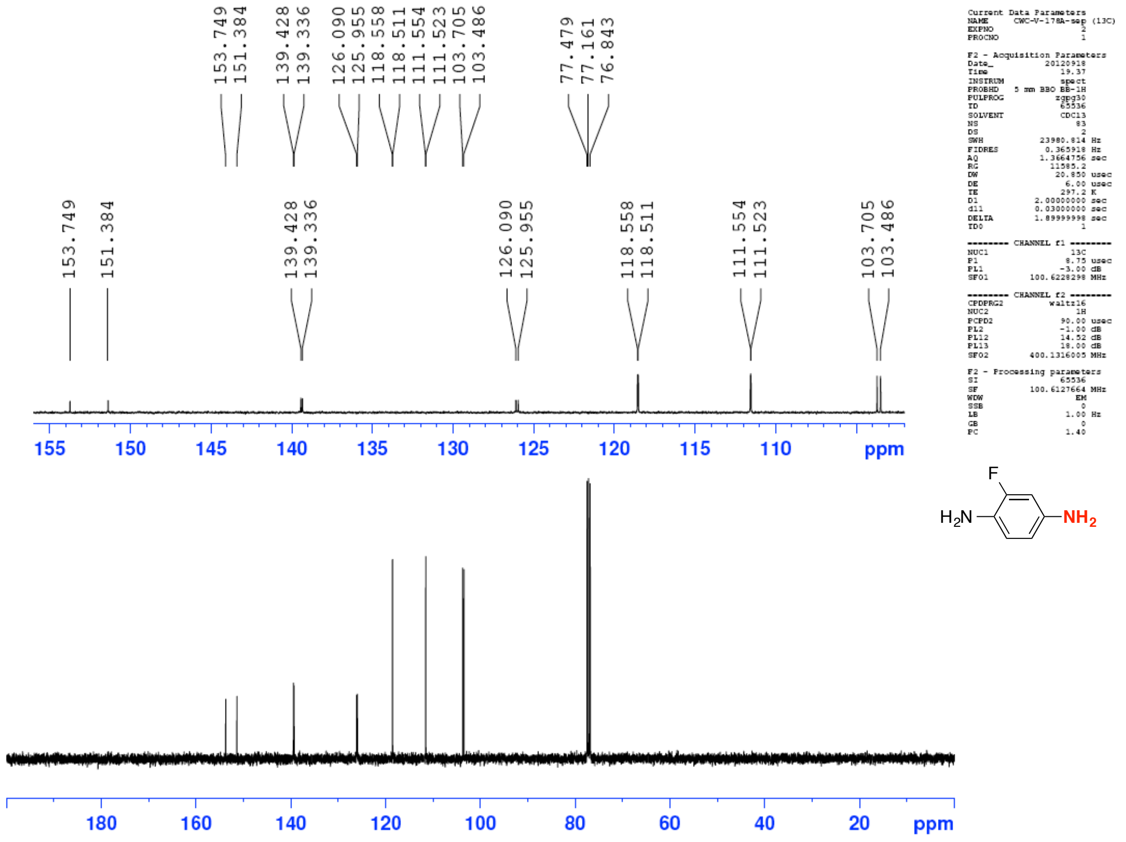


```
Current Data Parameters
NAME      CWC-V-272B-sep (C13)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121101
Time               22.52
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDC13
NS                   885
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664256 sec
RG                 16384
DW                20.850 usec
DE                  6.00 usec
TE                 297.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1
SFO1         100.6228298 MHz
NUC1                 13C
P1                  8.75 usec
PLW1         -1.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                 65536
SF           100.6127617 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

^{1}H and ^{13}C NMR of 2-Fluorobenzene-1,4-diamine (**4t**)

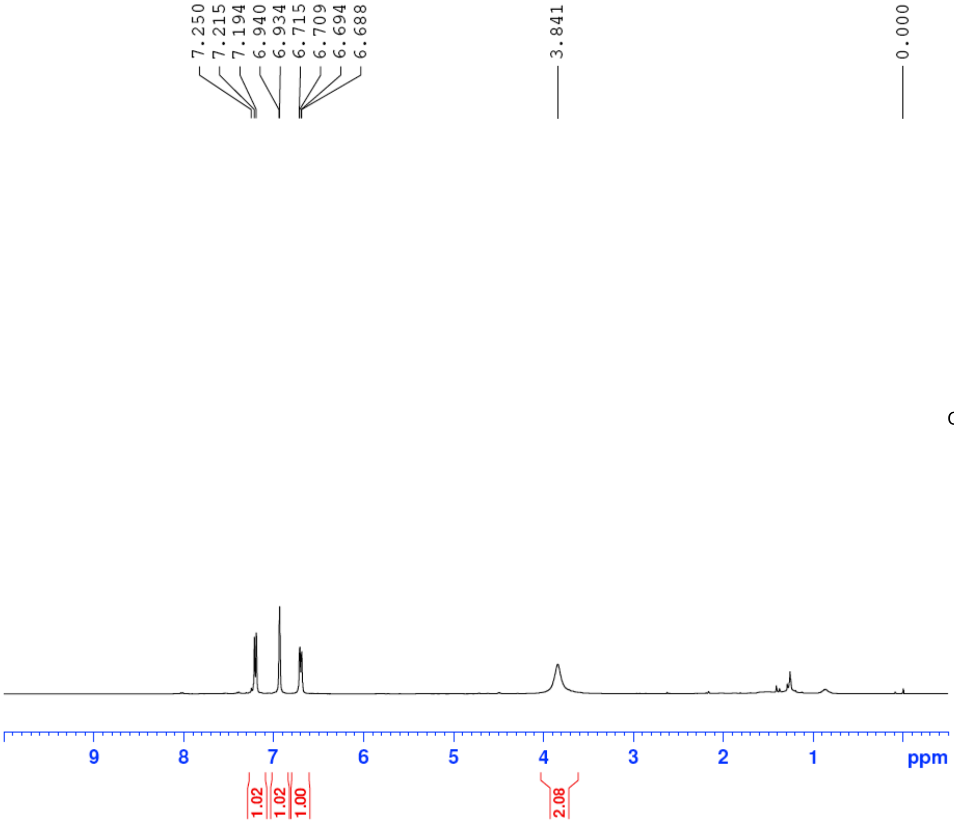


```
Current Data Parameters
NAME      CWC-V-178B-sep (1H)
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120918
Time                 15.51
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      21
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                      57
DW                  60.400 usec
DE                    6.00 usec
TE                   297.2 K
D1              3.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300102 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

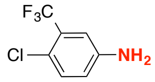


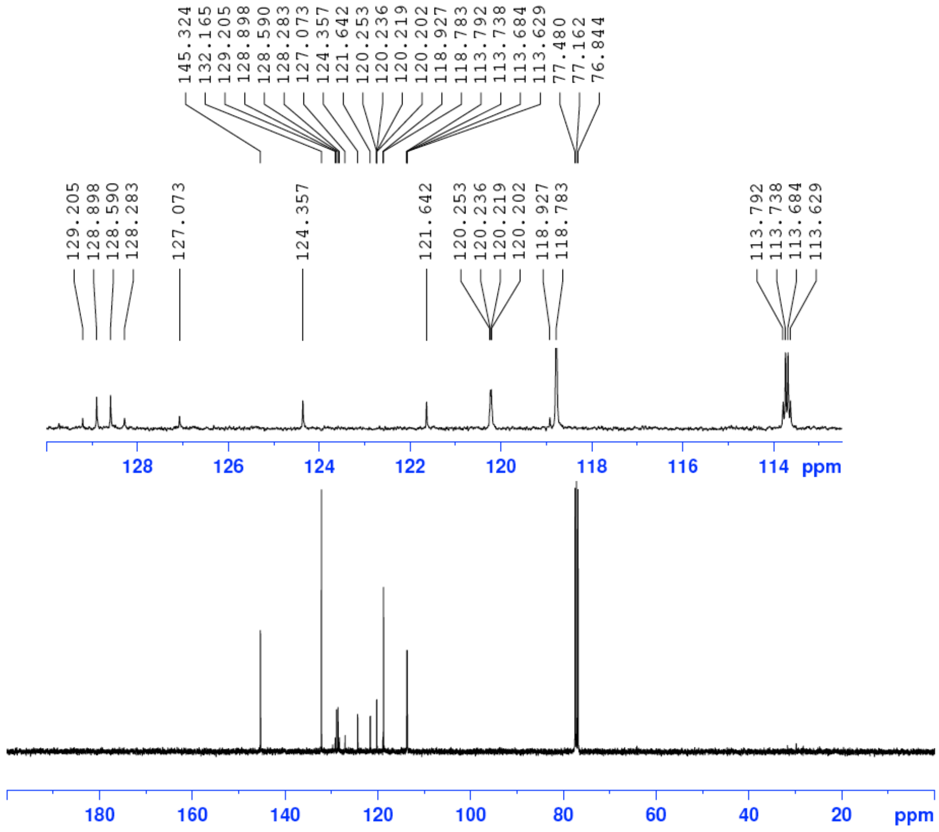
```
Current Data Parameters
NAME      CWC-V-178A-sep (13C)
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120918
Time                 19.37
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      83
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                 11585.2
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127664 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR of 4-Chloro-3-(trifluoromethyl)aniline (**4u**)

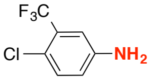


```
Current Data Parameters
NAME     CWC-V-238B-sep (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121026
Time                 22.45
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      40
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    45.3
DW                  60.400 usec
DE                    6.00 usec
TE                   297.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300139 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

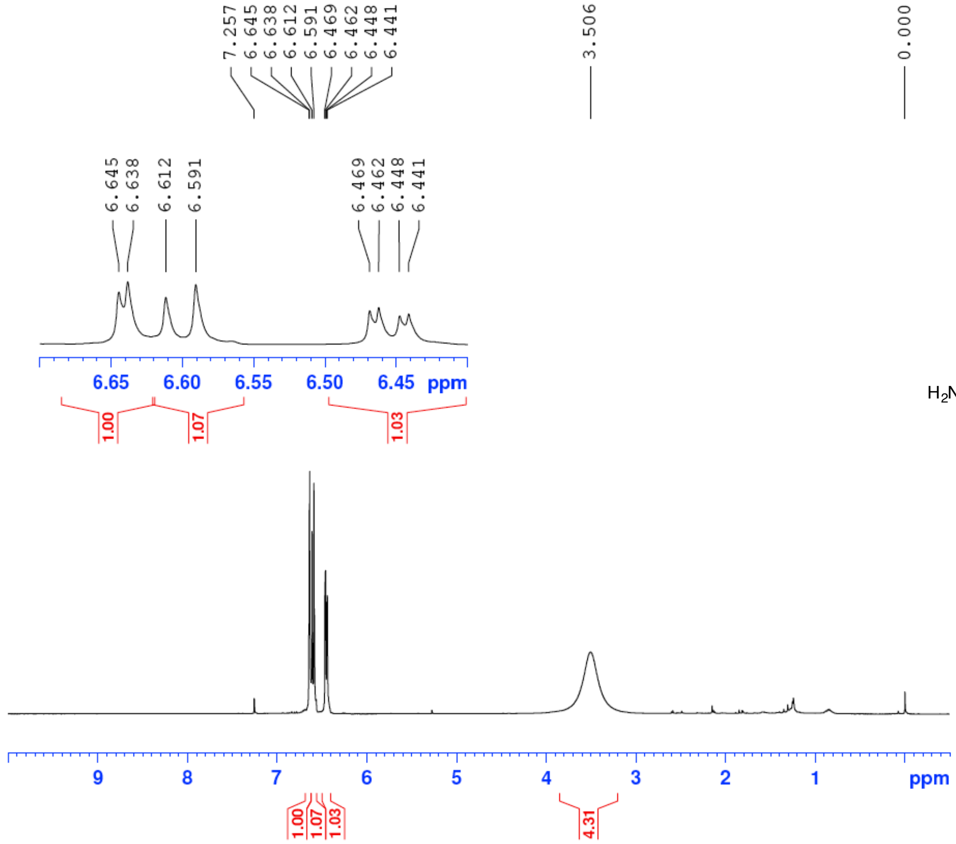




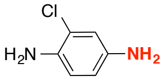
```
Current Data Parameters
NAME     CWC-V-238B-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121026
Time                 22.52
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1880
DS                       2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                 18390.4
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127596 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

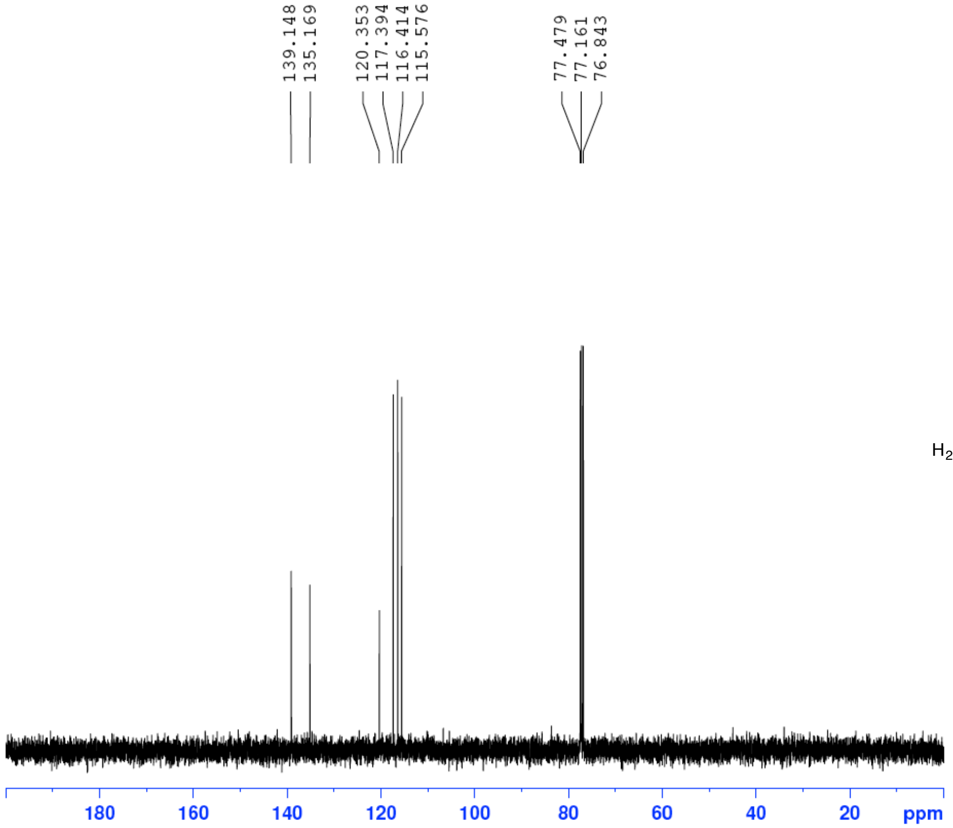


^{1}H and ^{13}C NMR of 2-Chlorobenzene-1,4-diamine (**4v**)

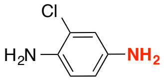


```
Current Data Parameters
NAME     CWC-V-233A-sep (3) (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121017
Time                 0.45
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     34
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   71.8
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300112 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

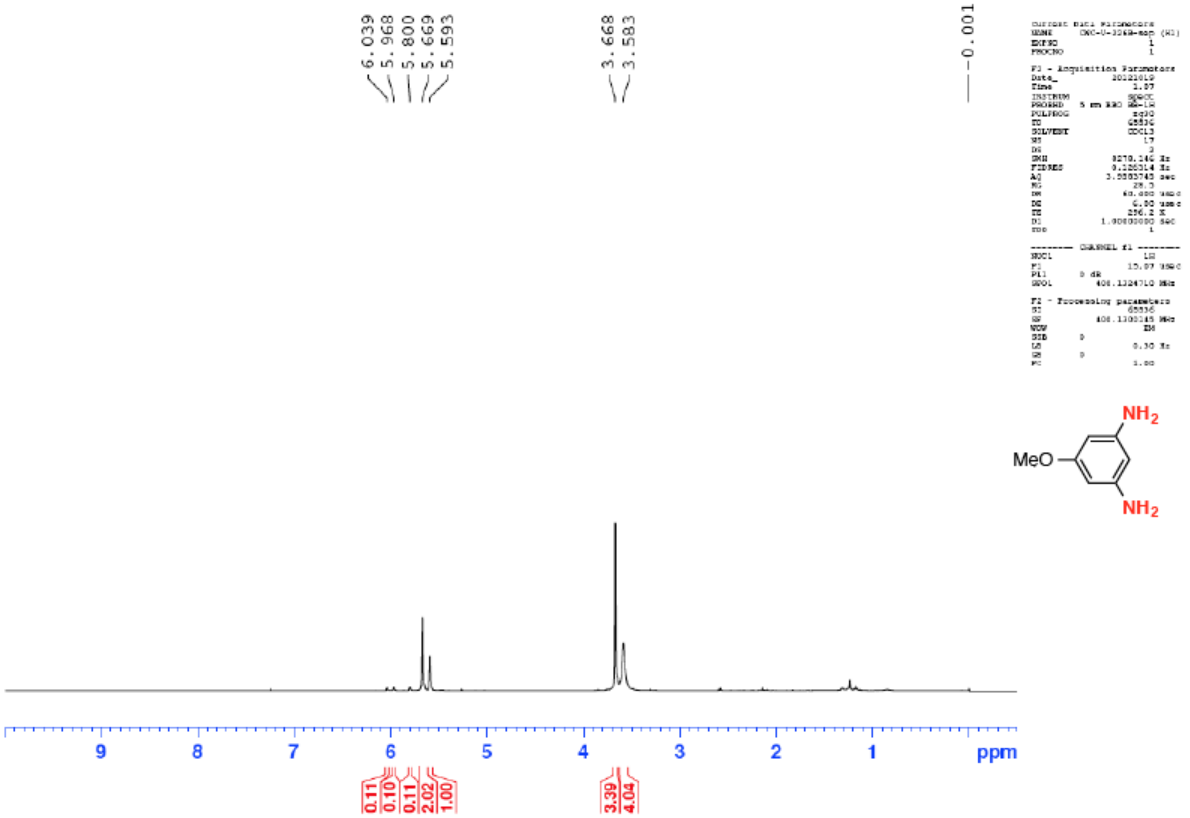


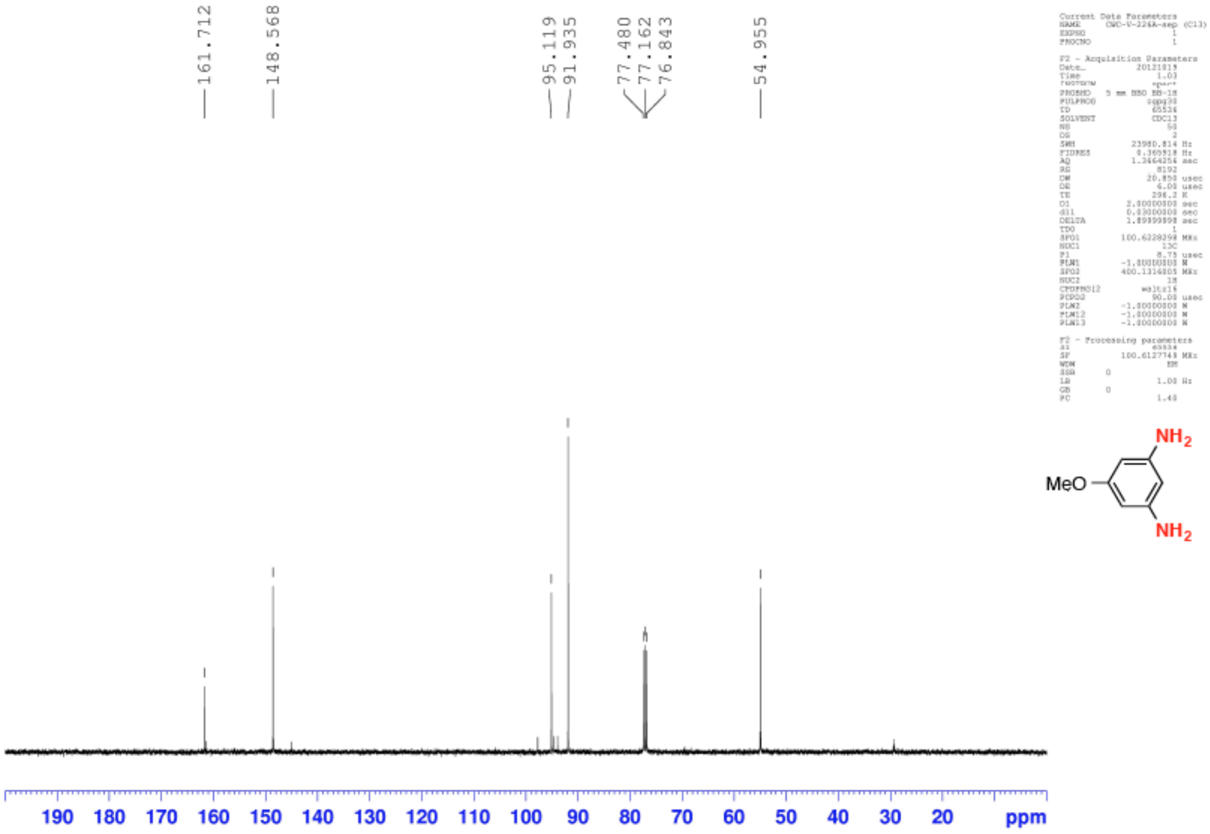


```
Current Data Parameters
NAME     CWC-V-233A-sep (3) (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121017
Time                 0.50
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     42
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                14596.5
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127696 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

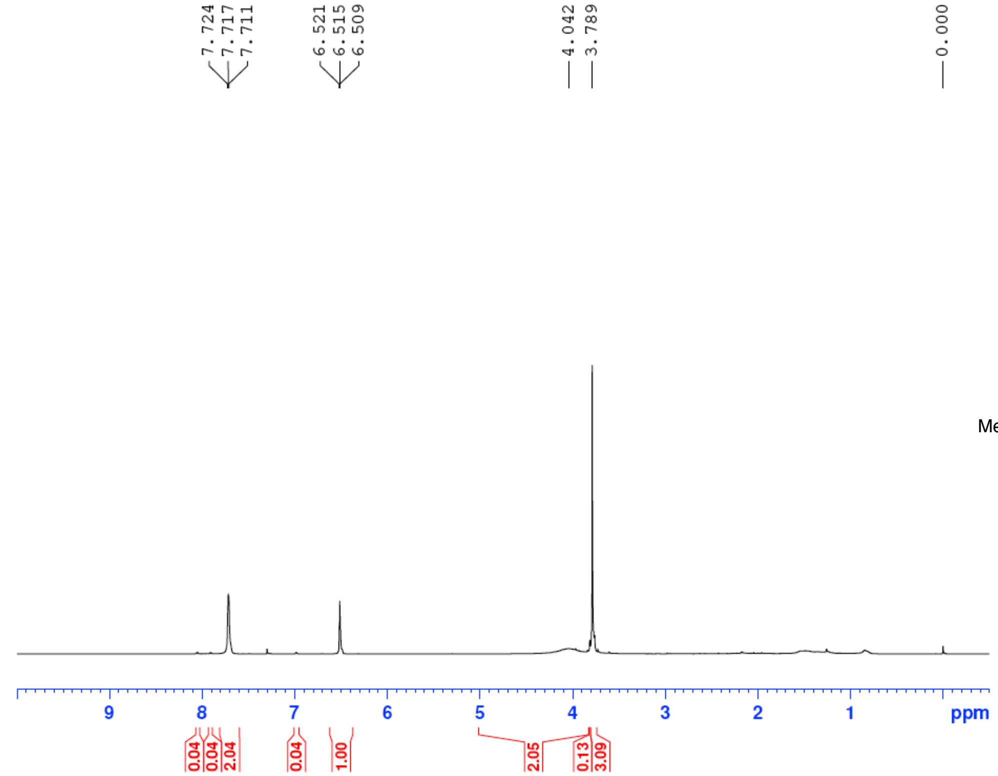


^{1}H and ^{13}C NMR of 5-Methoxybenzene-1,3-diamine (**4w**)

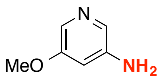


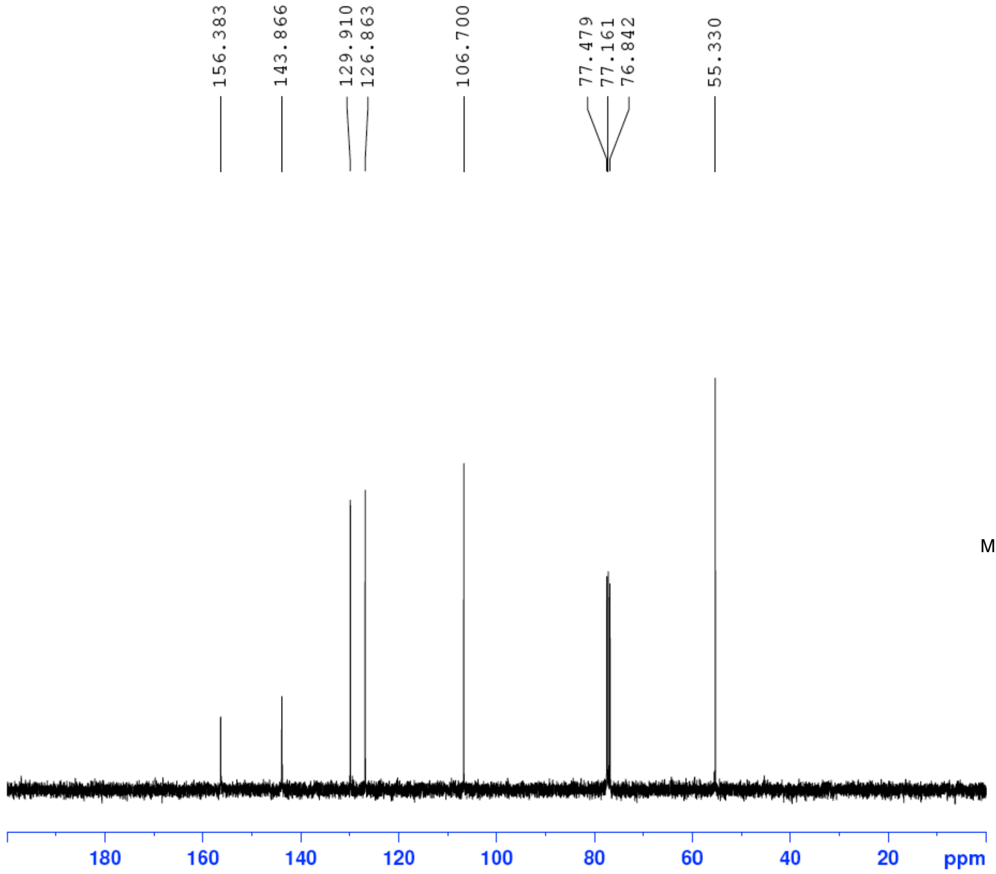


^{1}H and ^{13}C NMR of 3-Amino-5-methoxypyridine (**5a**)

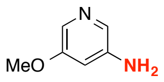


```
Current Data Parameters
NAME      CWC-V-224B-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121011
Time                23.50
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     39
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                     57
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1      0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1299944 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

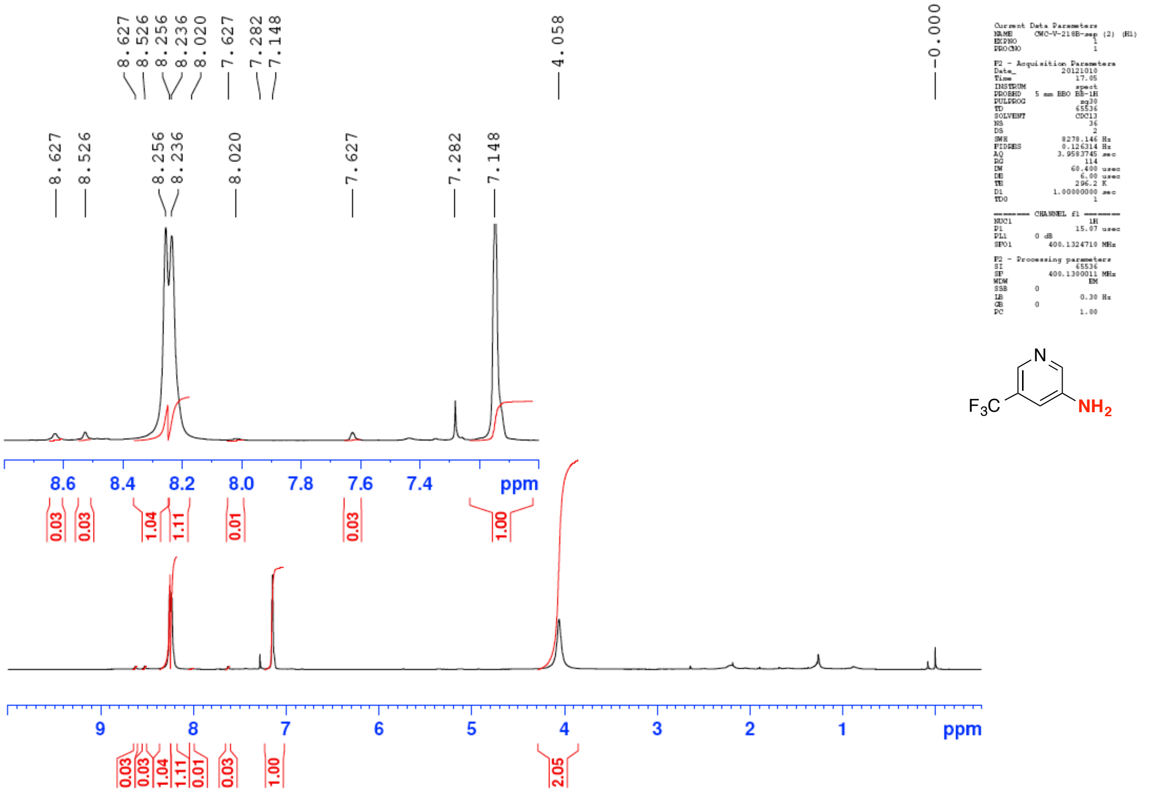




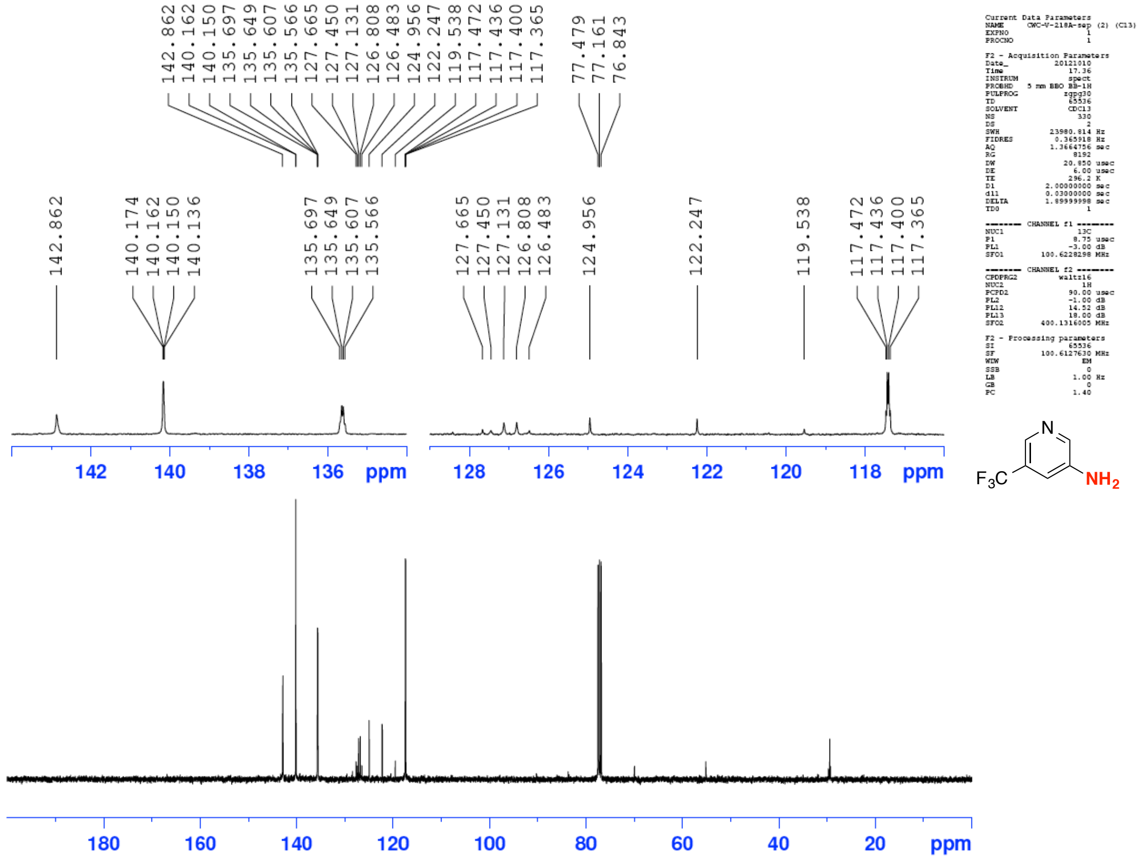
```
Current Data Parameters
NAME      CWC-V-224A-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121011
Time                23.42
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                18390.4
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127735 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



^{1}H and ^{13}C NMR of 3-Amino-5-(trifluoromethyl)pyridine (**5b**)

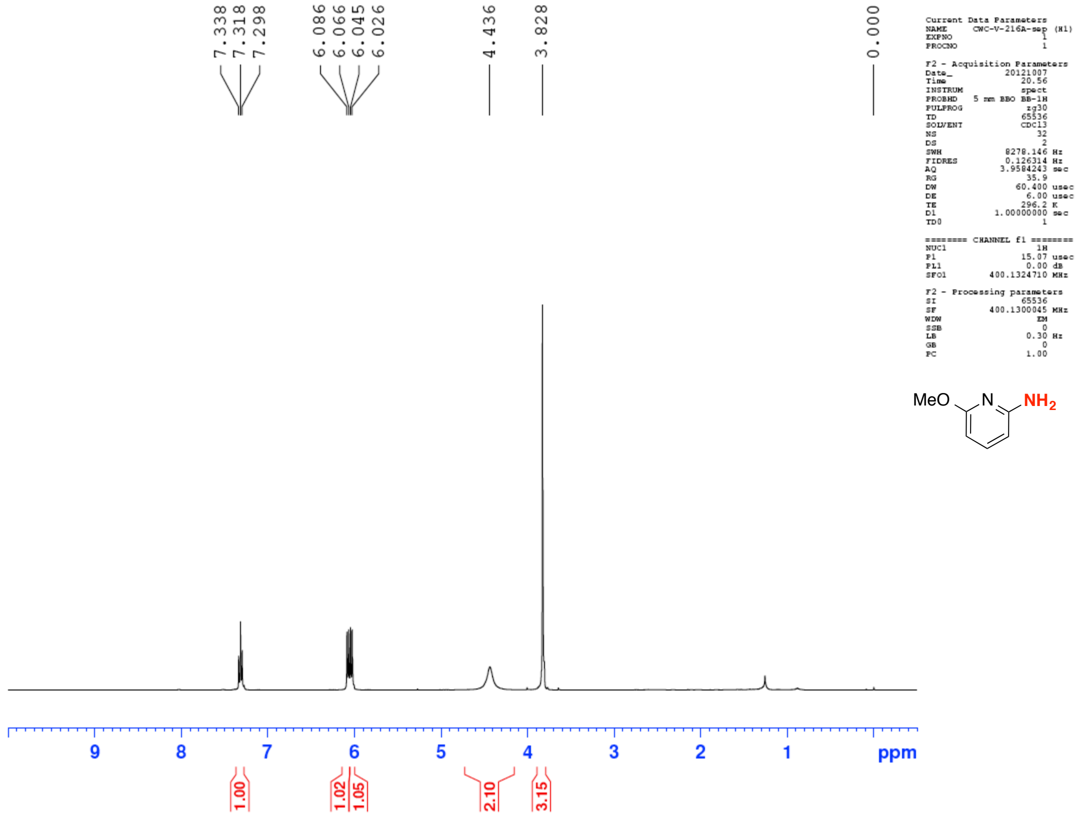


```
Current Data Parameters
NAME     CWC-V-218B-sep (2)  (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121010
Time                 17.05
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9583745 sec
RG                     114
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1      0 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF          400.1300011 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

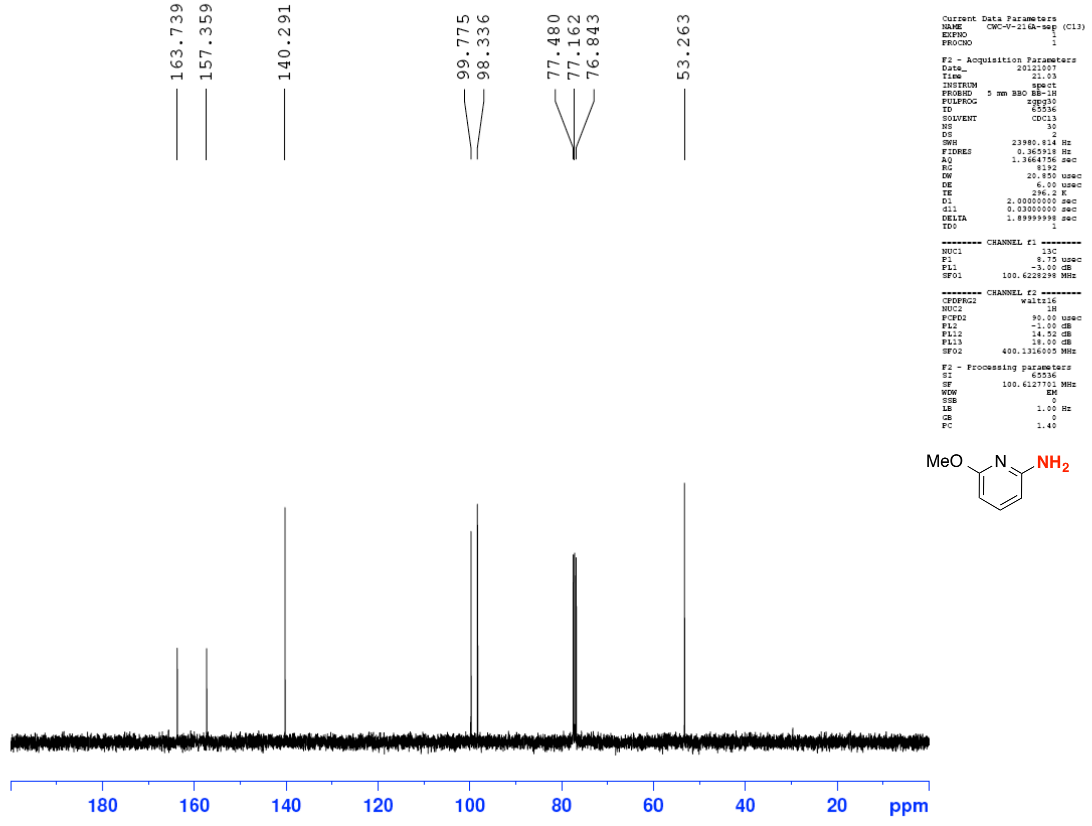


```
Current Data Parameters
NAME     CWC-V-218A-sep (2) (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121010
Time                 17.36
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    330
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF           100.6127630 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of 2-Amino-6-methoxypyridine (**5c**)

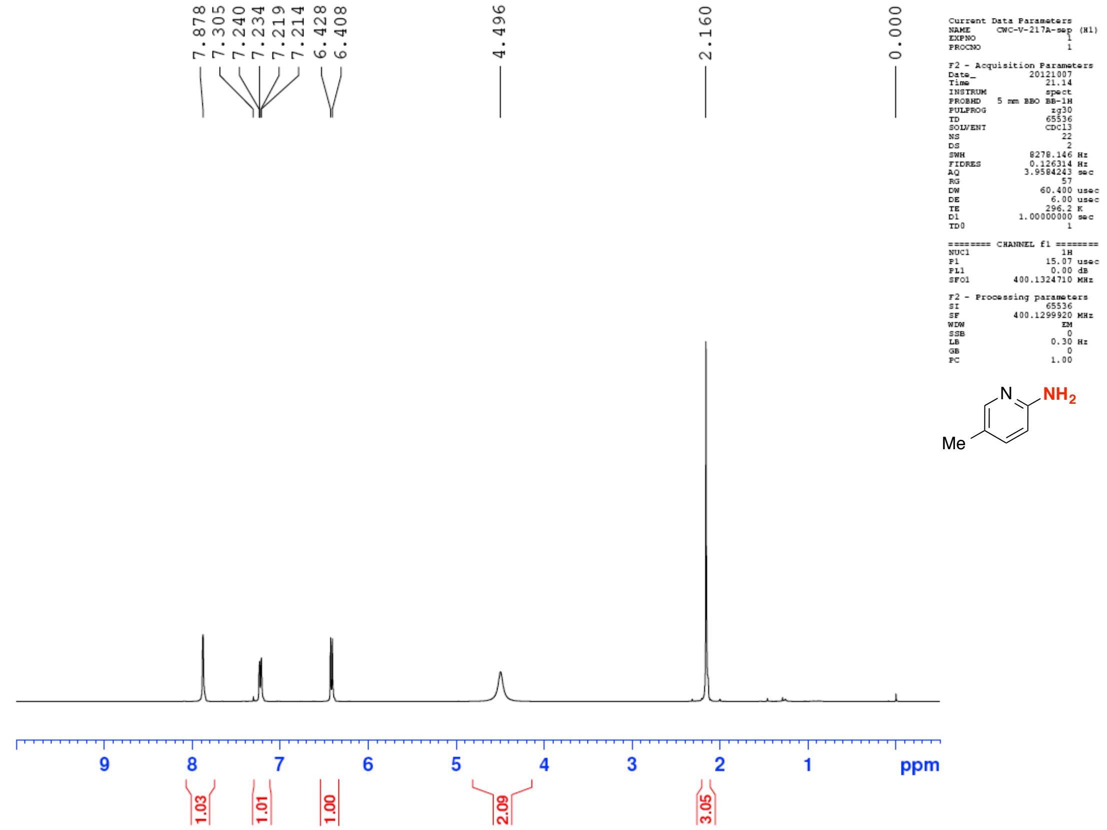


```
Current Data Parameters
NAME     CWC-V-216A-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121007
Time                20.56
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   35.9
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300045 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

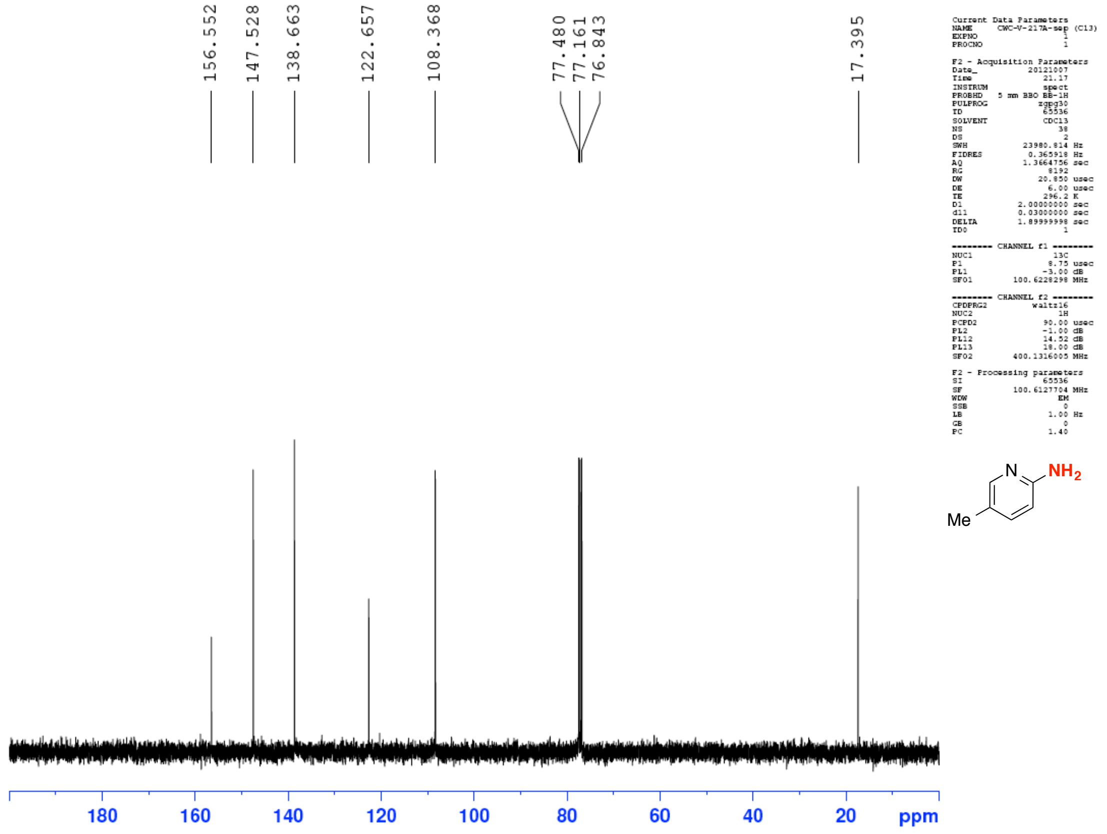


```
Current Data Parameters
NAME     CWC-V-216A-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121007
Time                21.03
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     30
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127701 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of 2-Amino-5-methylpyridine (**5d**)

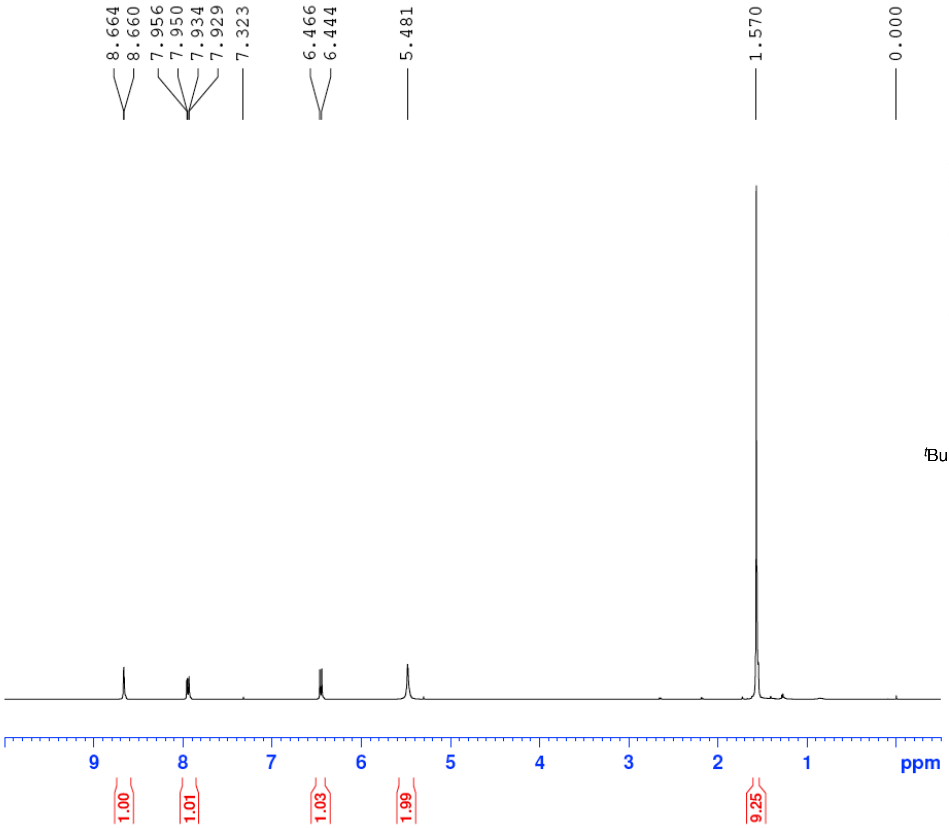


```
Current Data Parameters
NAME     CWC-V-217A-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121007
Time                21.14
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     22
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                     57
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1299920 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

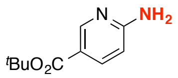


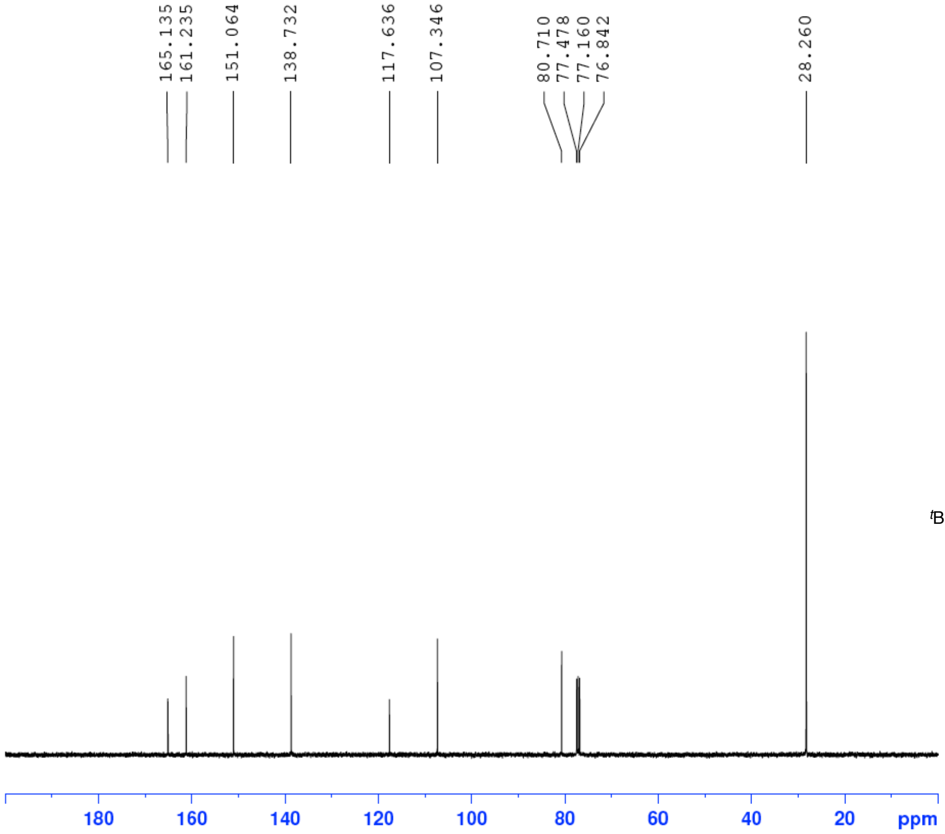
```
Current Data Parameters
NAME     CWC-V-217A-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121007
Time                21.17
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     38
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127704 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of *tert*-Butyl 6-aminonicotinate (**5e**)

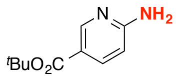


```
Current Data Parameters
NAME     CWC-V-225A-sep (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121011
Time                 23.31
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      17
DS                       2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                    35.9
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF           400.1299846 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

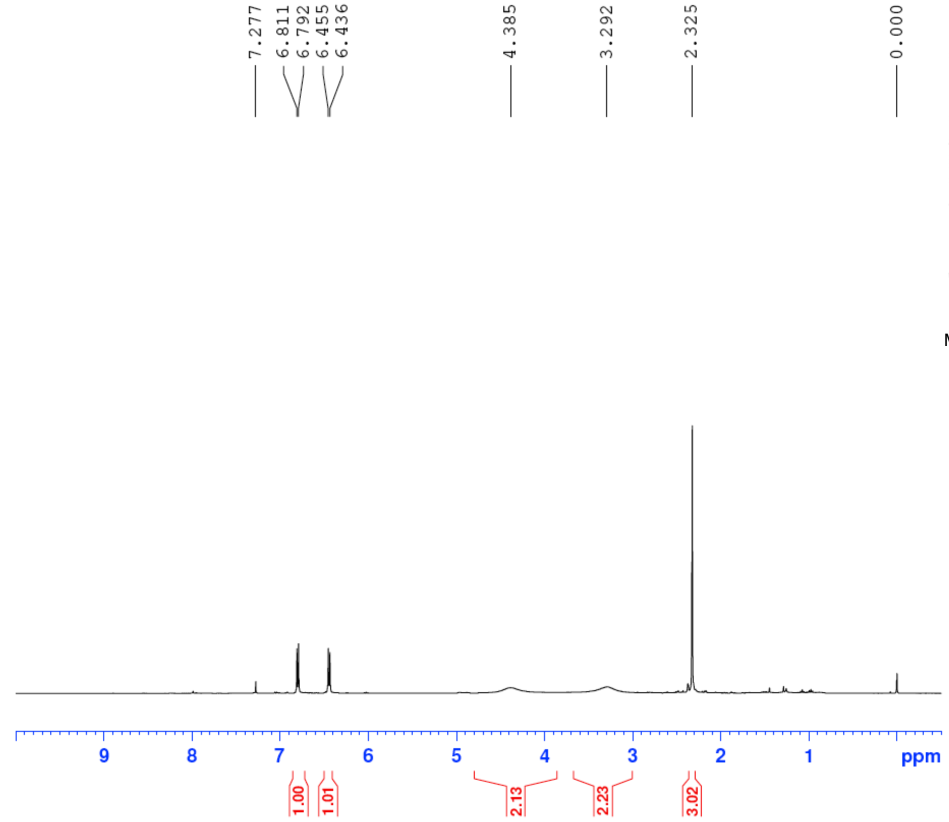




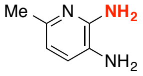
```
Current Data Parameters
NAME     CWC-V-225A-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121011
Time                 23.34
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      36
DS                       2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                   13004
DW                  20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                      1

-------- CHANNEL f1 --------
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1         100.6228298 MHz

-------- CHANNEL f2 --------
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF           100.6127670 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

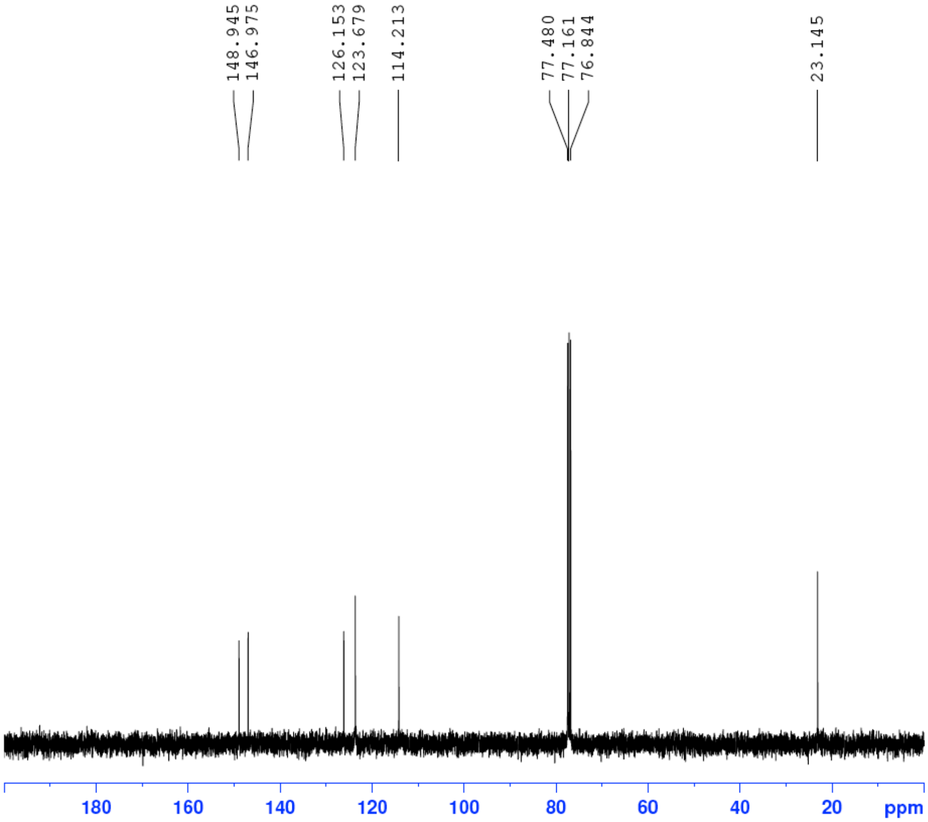


^{1}H and ^{13}C NMR of 6-Methylpyridine-2,3-diamine (**5f**)

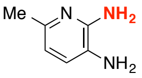


```
Current Data Parameters
NAME      CWC-V-219A-sep (2) (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121009
Time                23.53
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     34
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   80.6
DW                 60.400 usec
DE                   6.00 usec
TE                  297.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300022 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

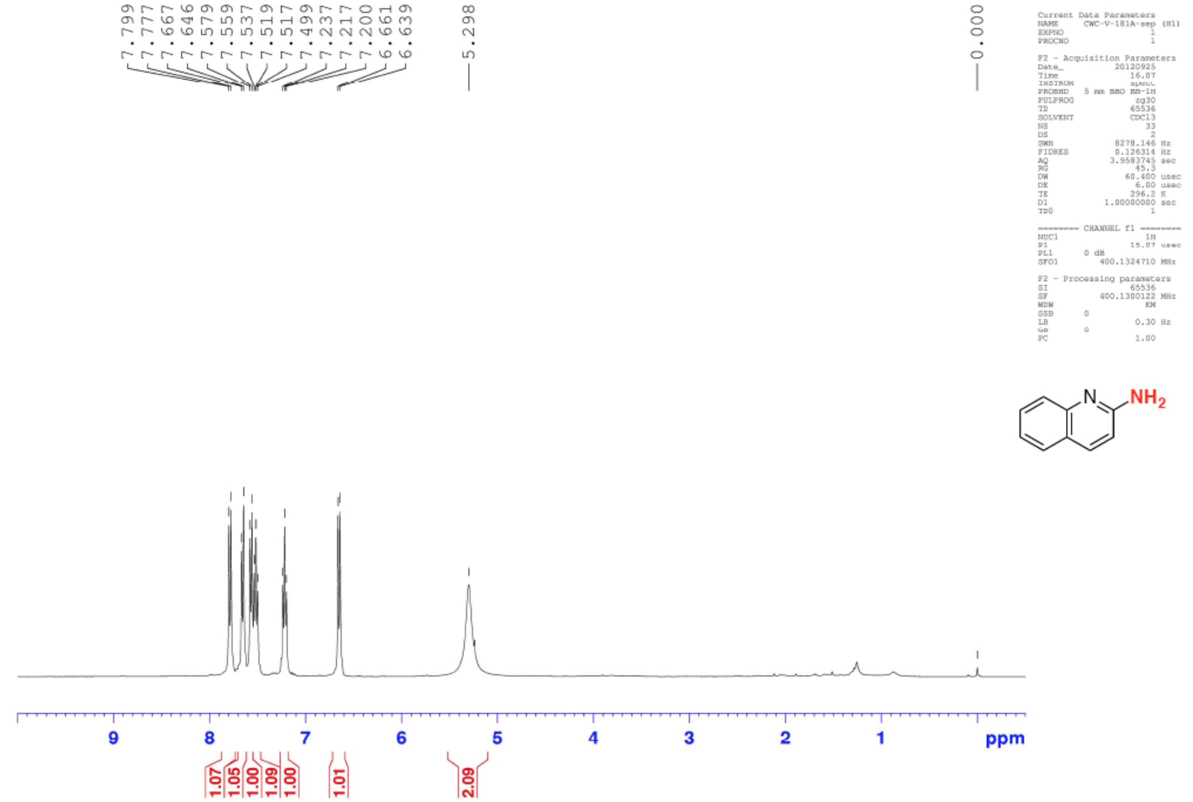




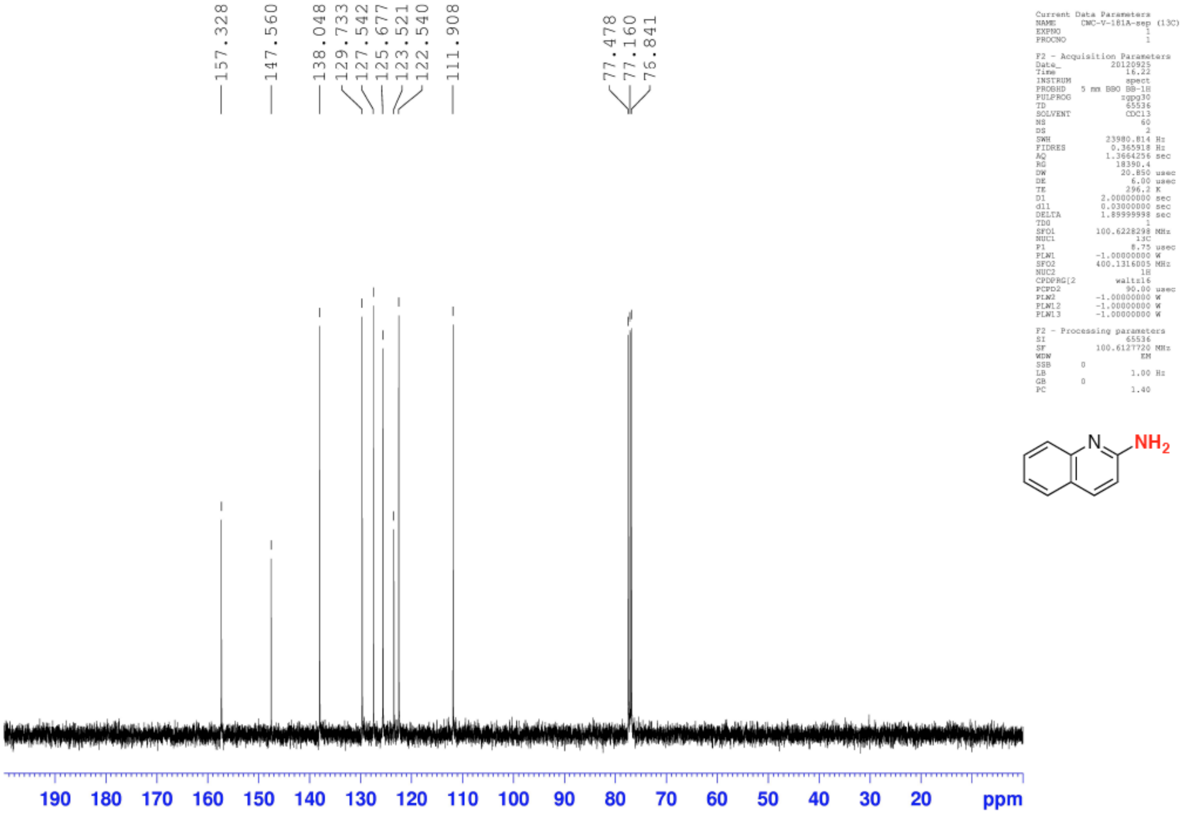
```
Current Data Parameters
NAME      CWC-V-219A-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121009
Time                 0.10
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     42
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127633 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



^{1}H and ^{13}C NMR of 2-Aminoquinoline (**5g**)

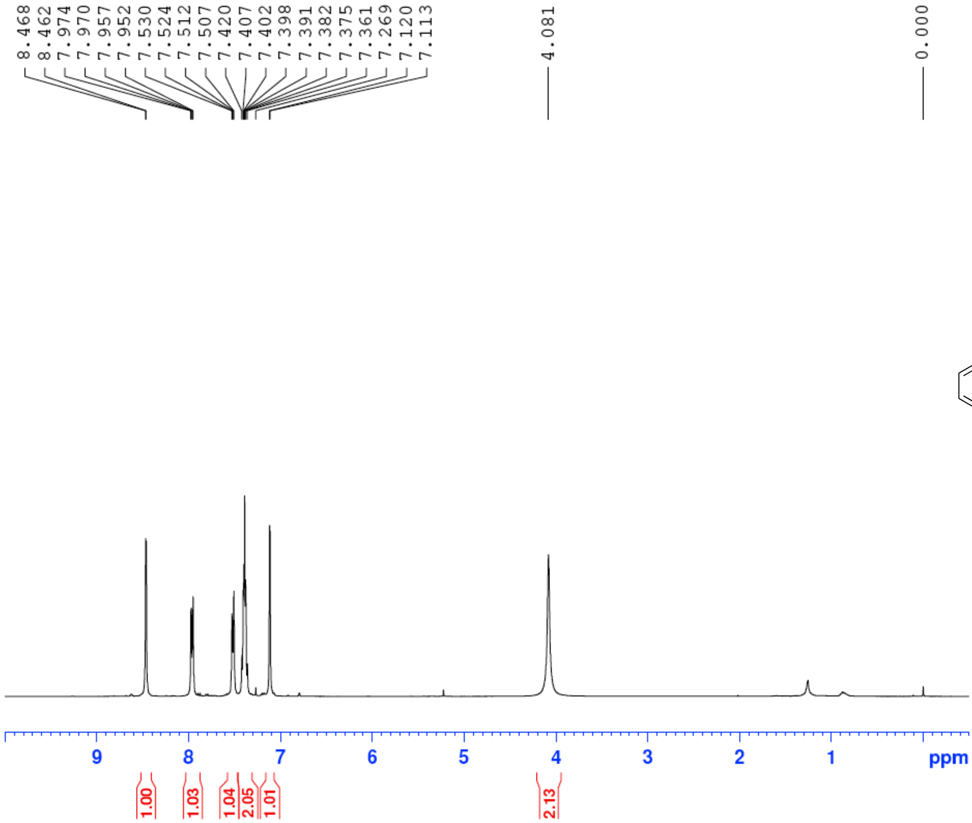


```
Current Data Parameters
NAME     CWC-V-181A-sep (H1)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120925
Time                  16.07
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       33
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                     45.3
DW                   60.400 usec
DE                     6.00 usec
TE                    296.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.07 usec
PL1      0 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF              400.1300122 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

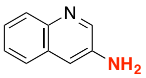


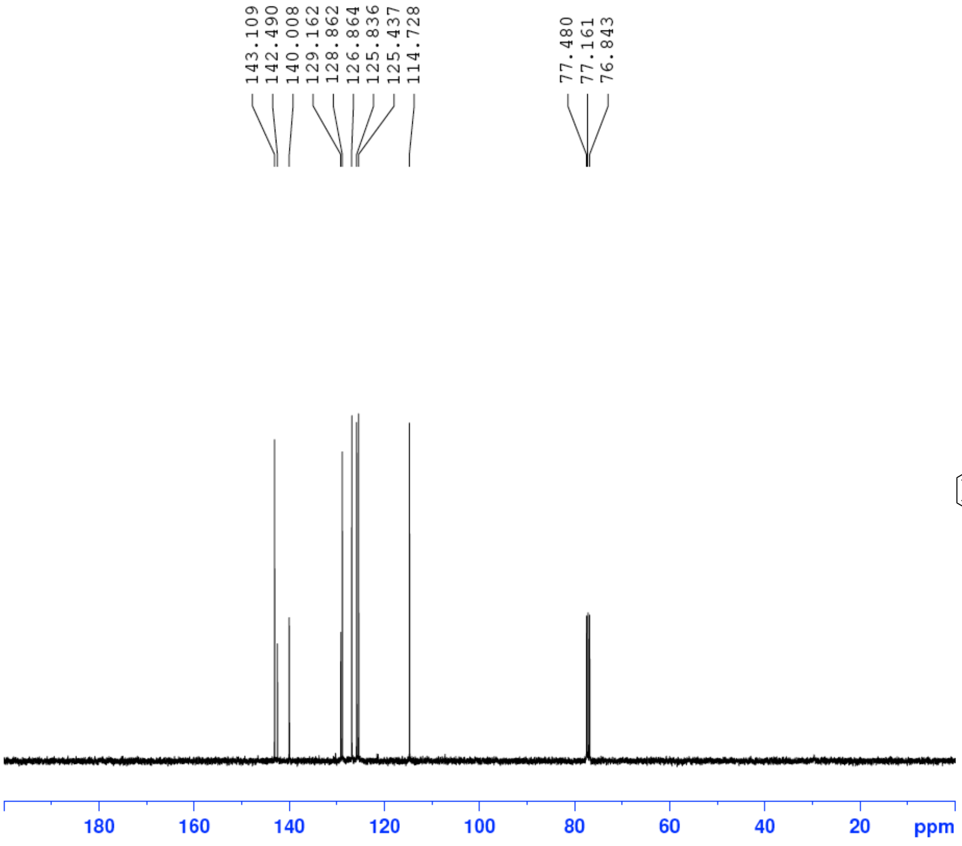
```
Current Data Parameters
NAME     CWC-V-181A-sep (13C)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120925
Time                  16.22
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       60
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664256 sec
RG                  18390.4
DW                   20.850 usec
DE                     6.00 usec
TE                    296.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1
SFO1            100.6228298 MHz
NUC1                    13C
P1                     8.75 usec
PLW1            -1.00000000 W
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W
PLW13           -1.00000000 W

F2 - Processing parameters
SI                    65536
SF              100.6127720 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

^{1}H and ^{13}C NMR of 3-Aminoquinoline (**5h**)

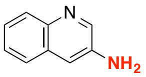


```
Current Data Parameters
NAME     CWC-V-180A-sep (1H)
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120919
Time               0.56
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                 35.9
DW               60.400 usec
DE                 6.00 usec
TE                297.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.07 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                65536
SF          400.1300060 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

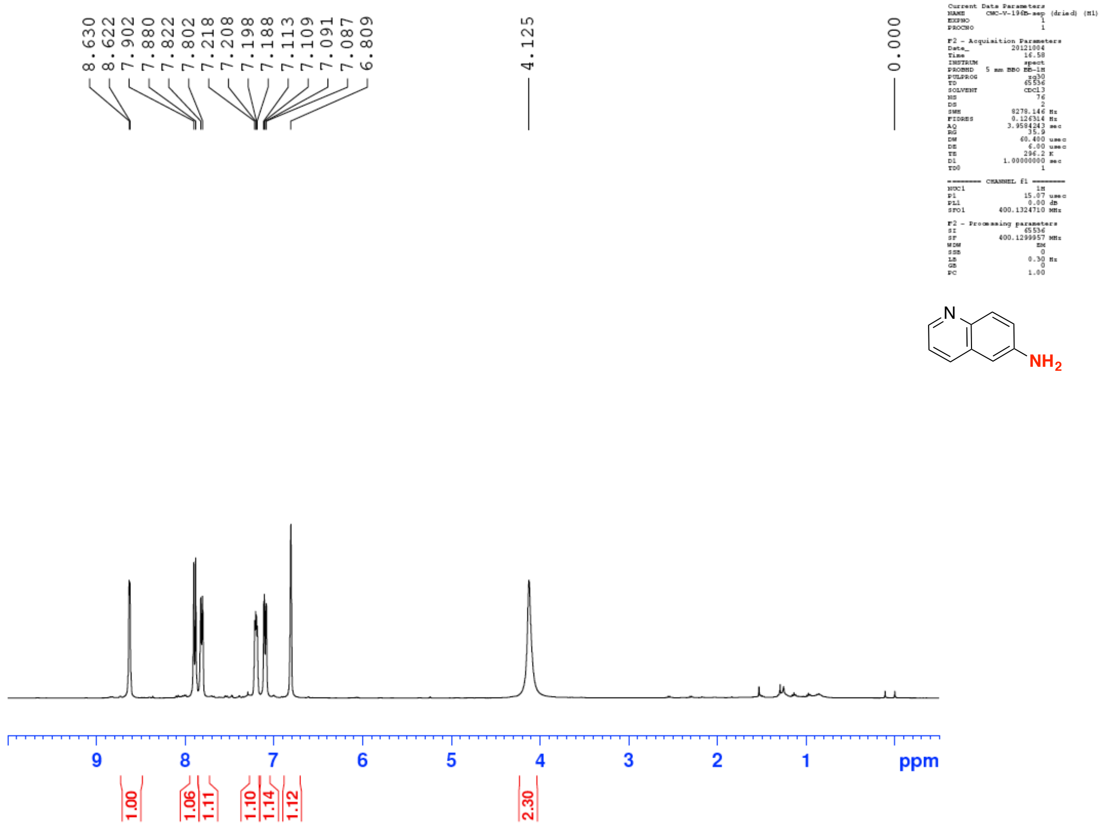


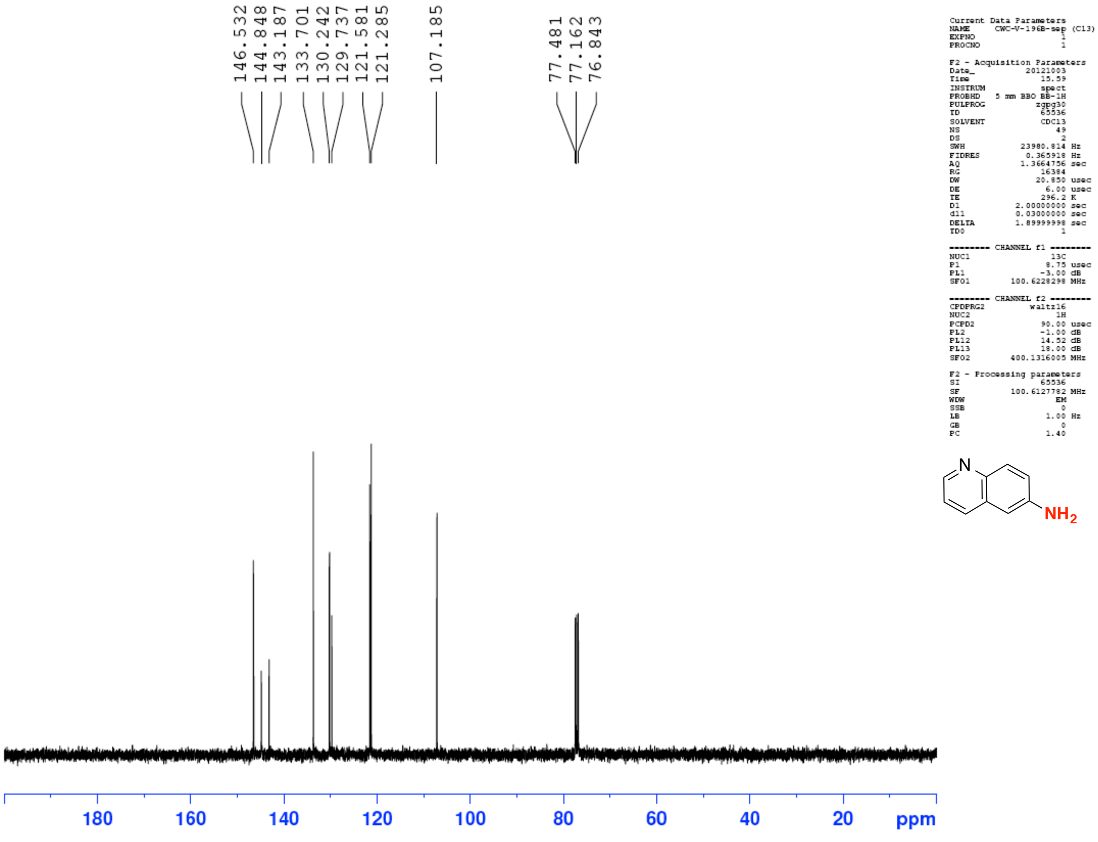


```
Current Data Parameters
NAME     CWC-V-180A-sep (13C)
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120919
Time               1.00
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   66
DS                    2
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ            1.3664756 sec
RG               5792.6
DW               20.850 usec
DE                 6.00 usec
TE                297.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.75 usec
PL1               -3.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              14.52 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                65536
SF          100.6127779 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

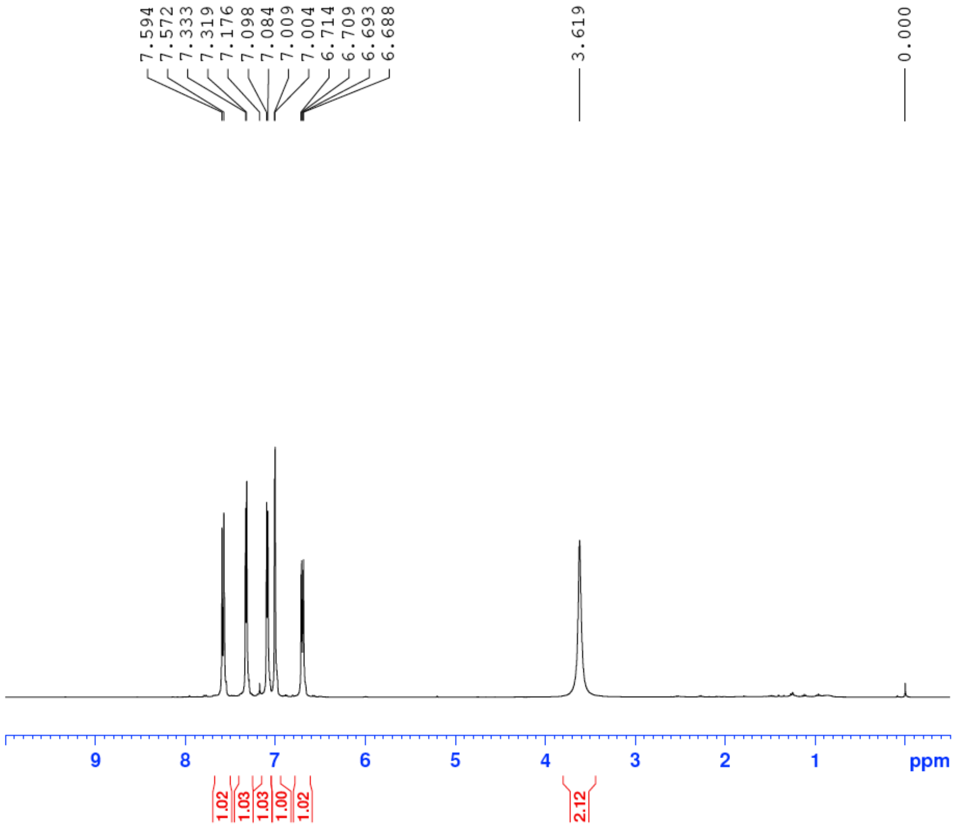


^{1}H and ^{13}C NMR of 6-Aminoquinoline (**5i**)

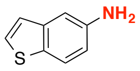


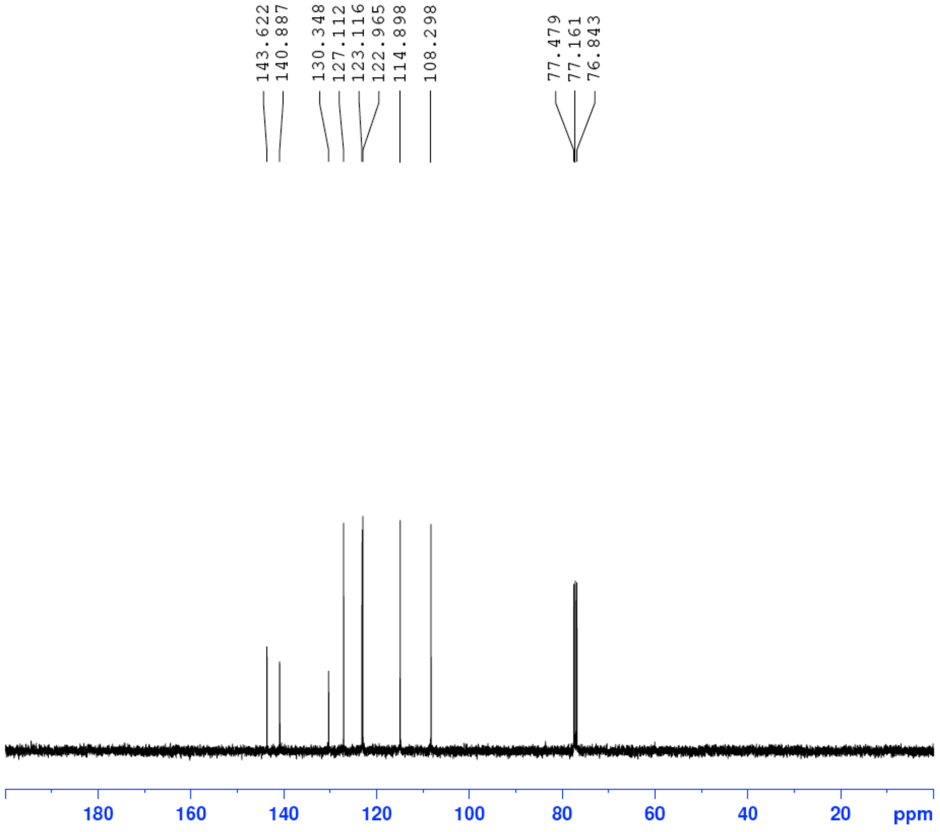


^{1}H and ^{13}C NMR of 5-Aminobenzothiophene (**5j**)

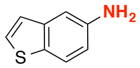


```
Current Data Parameters
NAME     CWC-V-195A-sep (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120925
Time               16.39
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  40.3
DW                60.400 usec
DE                  6.00 usec
TE                 296.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300433 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

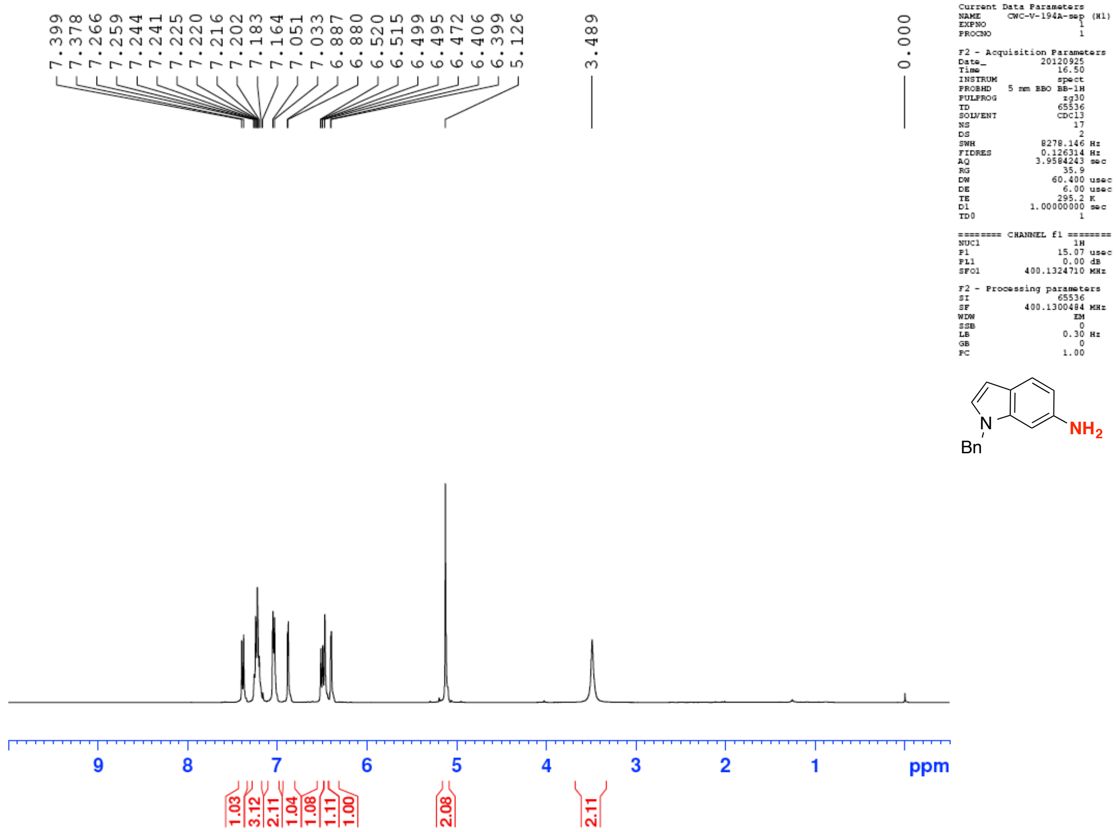




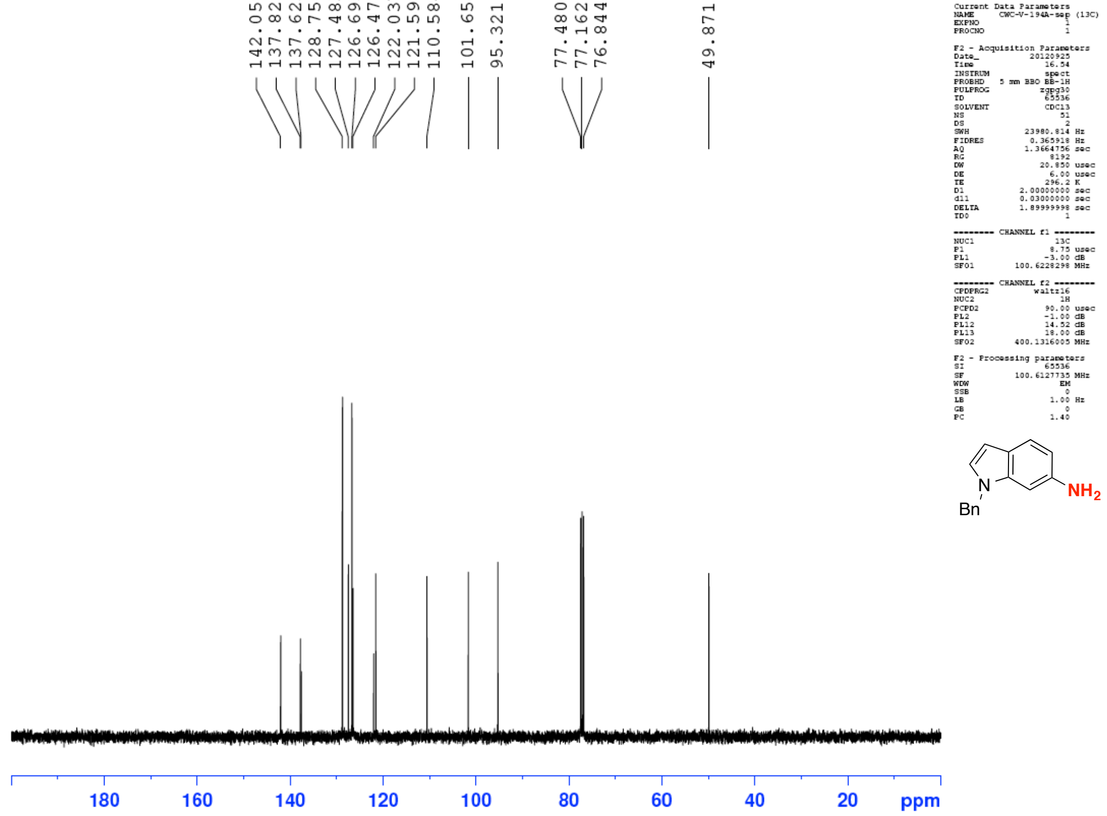
```
Current Data Parameters
NAME     CWC-V-195A-sep (C13)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120925
Time               16.42
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    39
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                7298.2
DW                20.850 usec
DE                  6.00 usec
TE                 296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127771 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



^{1}H and ^{13}C NMR of 6-Amino-1-benzyl-1*H*-indole (**5k**)

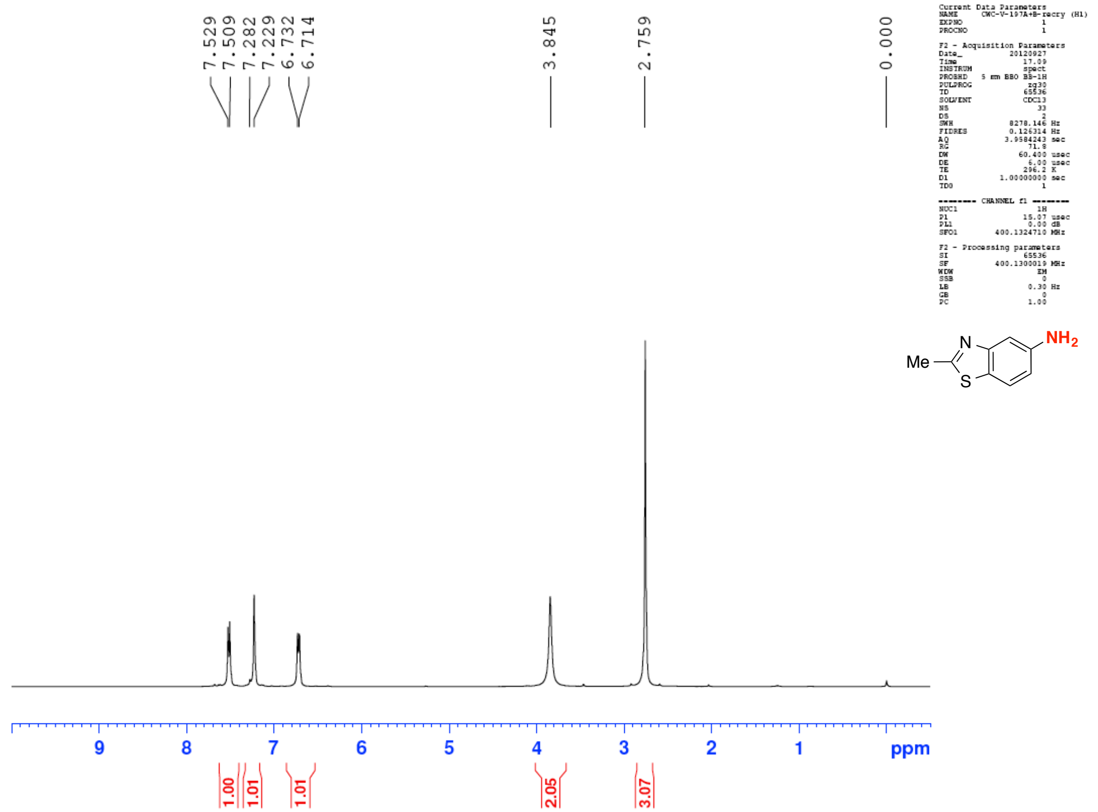


```
Current Data Parameters
NAME     CWC-V-194A-sep (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120925
Time               16.50
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    17
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  35.9
DW                60.400 usec
DE                  6.00 usec
TE                 295.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300484 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

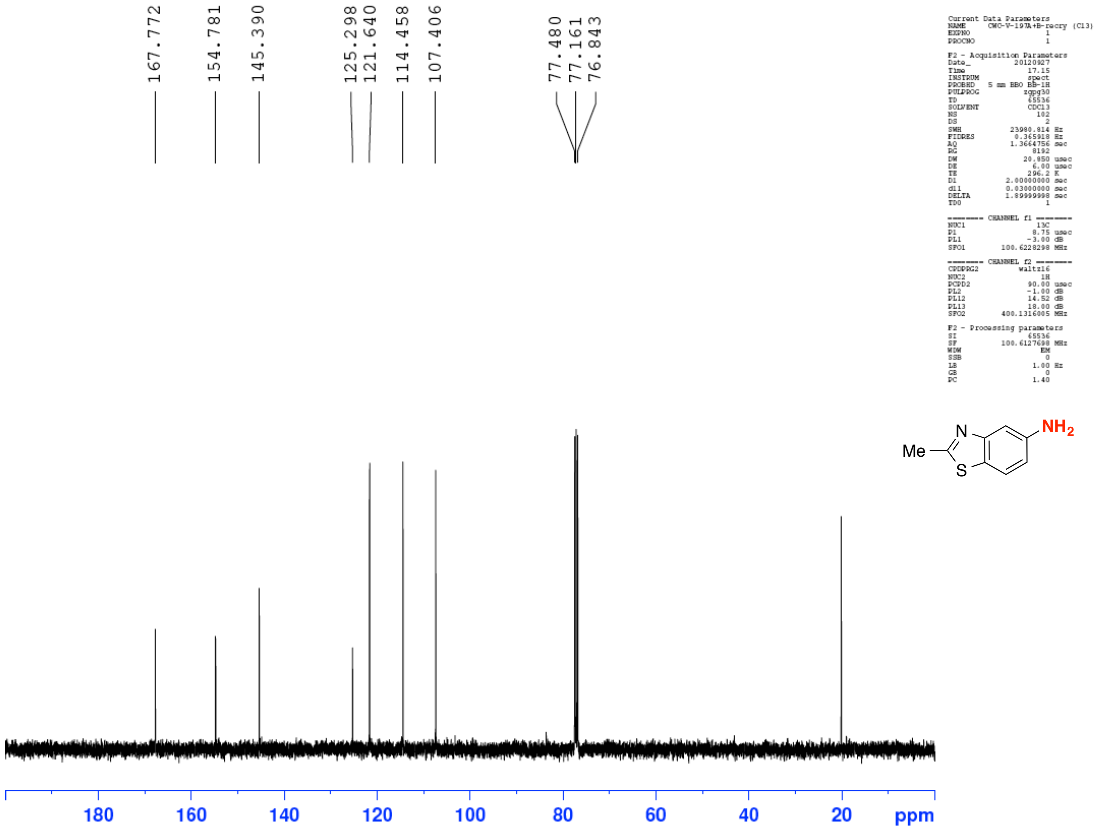


```
Current Data Parameters
NAME     CWC-V-194A-sep (13C)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120925
Time               16.54
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    51
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  8192
DW                20.850 usec
DE                  6.00 usec
TE                 296.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127735 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{1}H and ^{13}C NMR of 5-Amino-2-methylbenzothiazole (**5l**)

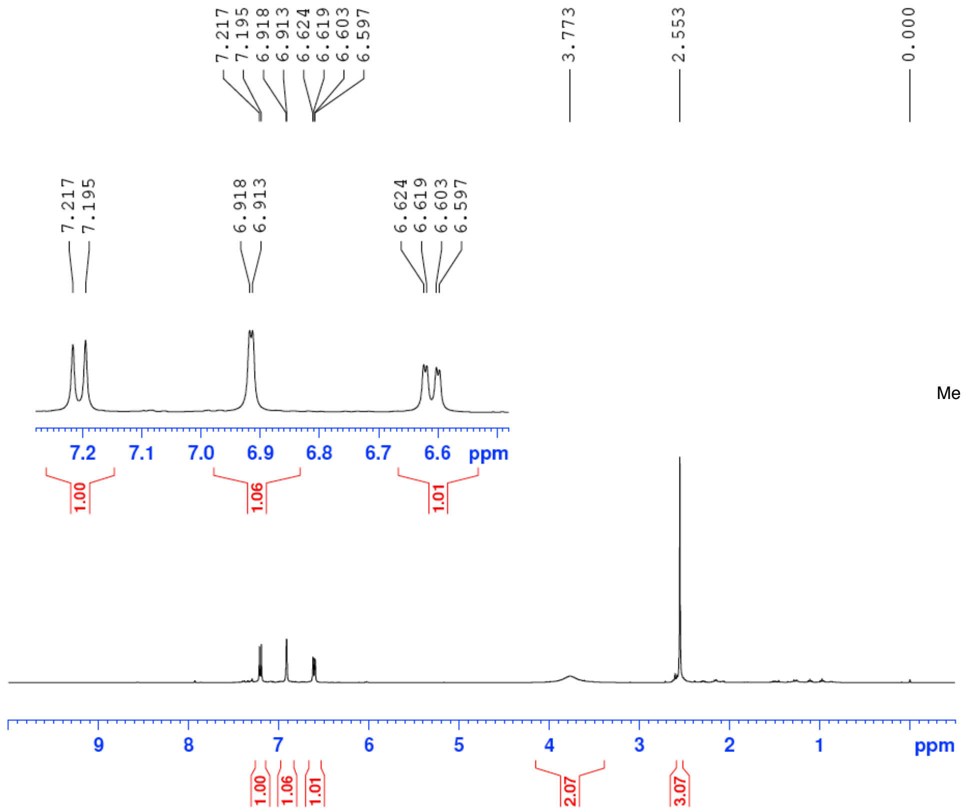


```
Current Data Parameters
NAME      CWC-V-197A+B-recry (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120927
Time                17.09
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     33
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   71.8
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300019 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

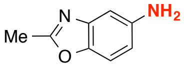


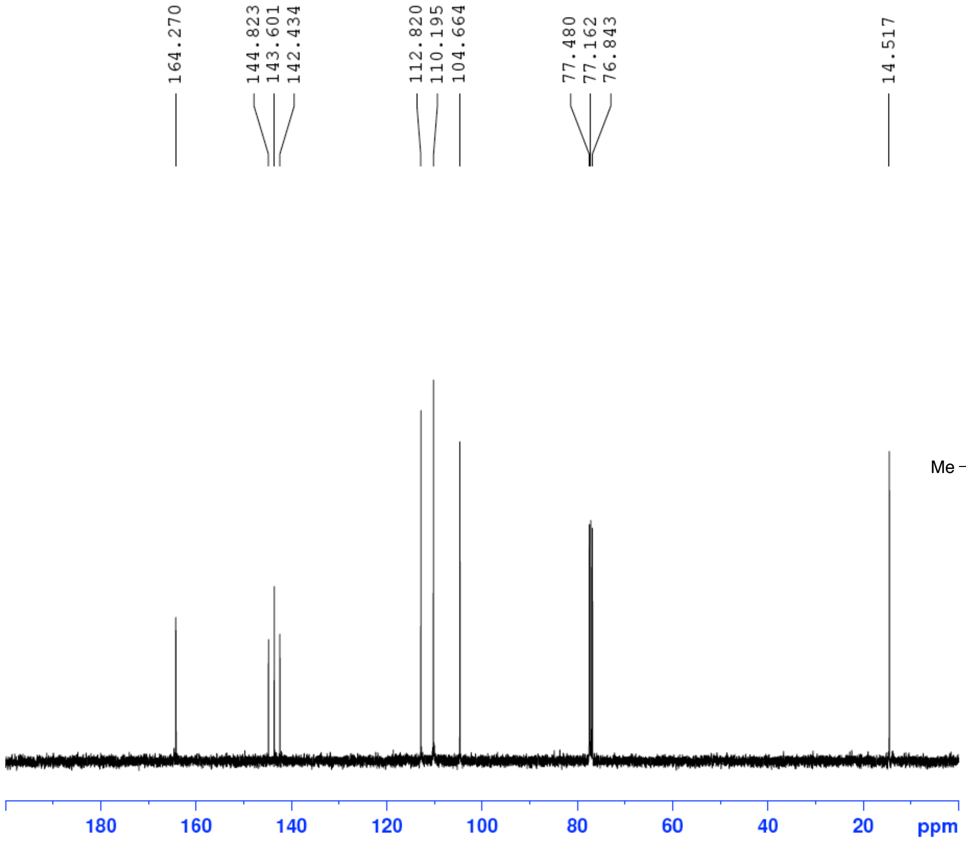
```
Current Data Parameters
NAME      CWC-V-197A+B-recry (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120927
Time                17.15
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    102
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127698 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of 5-Amino-2-methylbenzoxazole (**5m**)

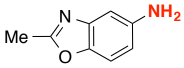


```
Current Data Parameters
NAME     CWC-V-189A-sep-2 (1H)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20120922
Time                3.39
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    47
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  40.3
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1299939 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

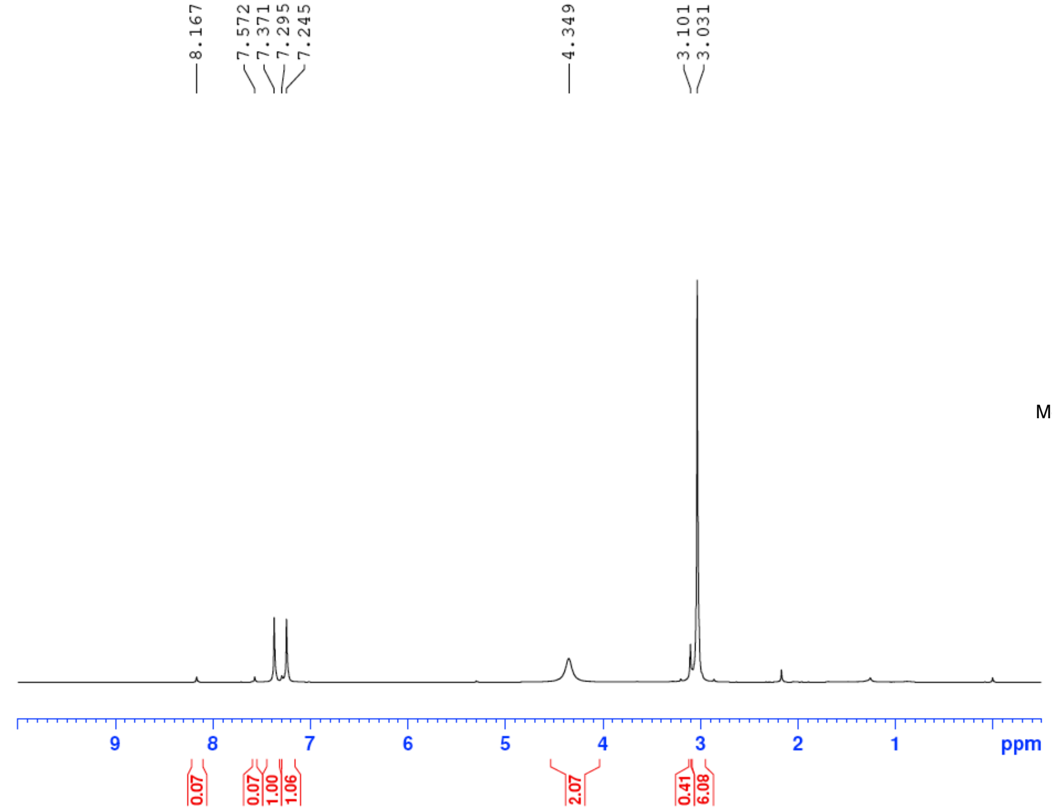




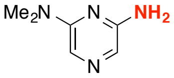
```
Current Data Parameters
NAME     CWC-V-189A-sep-2 (13C)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20120922
Time                3.45
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    70
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                  8192
DW                20.850 usec
DE                  6.00 usec
TE                 297.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.75 usec
PL1                -3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               14.52 dB
PL13               18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 65536
SF           100.6127699 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

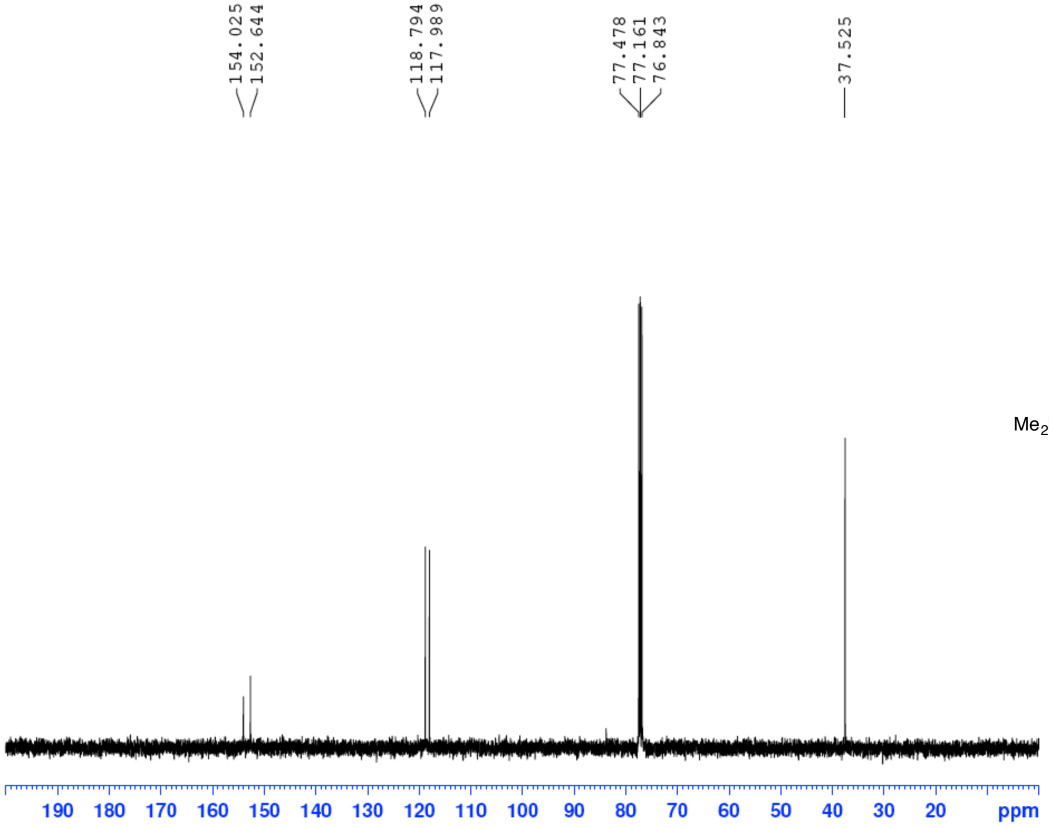


^{1}H and ^{13}C NMR of 2-Amino-6-dimethylamino)pyrazine (**5n**)

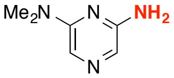


```
Current Data Parameters
NAME      CWC-V-191A-sep (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120925
Time                 16.29
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      34
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9583745 sec
RG                      57
DW                  60.400 usec
DE                    6.00 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1       0 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1299958 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

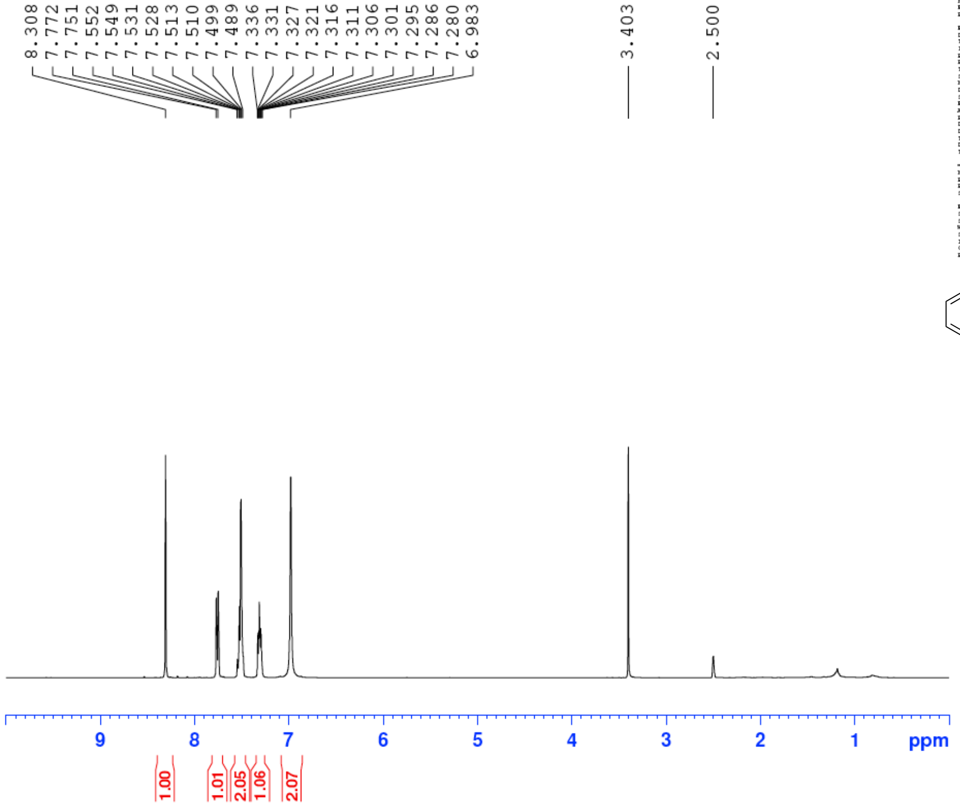




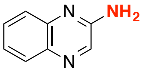
```
Current Data Parameters
NAME      CWC-V-191A-sep-3 (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120927
Time                  1.00
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     122
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664256 sec
RG                    8192
DW                  20.850 usec
DE                    6.00 usec
TE                   296.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1
SFO1           100.6228298 MHz
NUC1                   13C
P1                    8.75 usec
PLW1           -1.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                   65536
SF             100.6127592 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

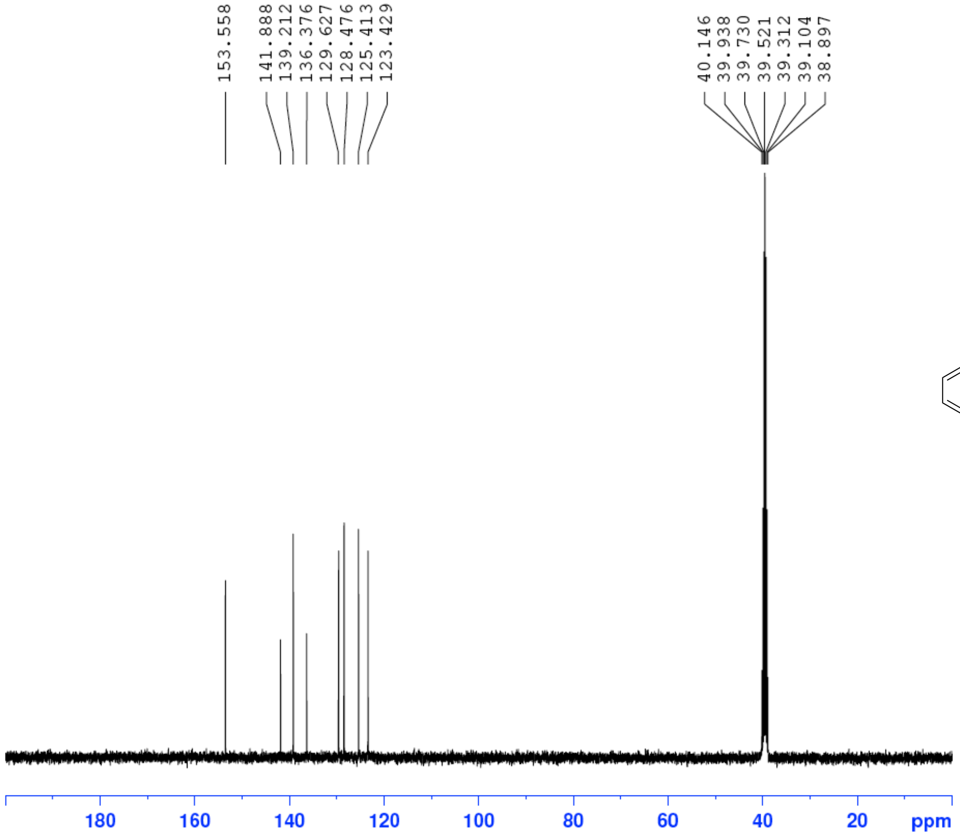


^{1}H and ^{13}C NMR of 2-Aminoquinoxaline (**5o**)

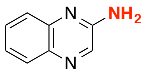


```
Current Data Parameters
NAME     CWO-V-170B-sep-3 (DMSO) (1H)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120922
Time                 3.24
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     31
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   90.5
DW                 60.400 usec
DE                   6.00 usec
TE                  297.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300022 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

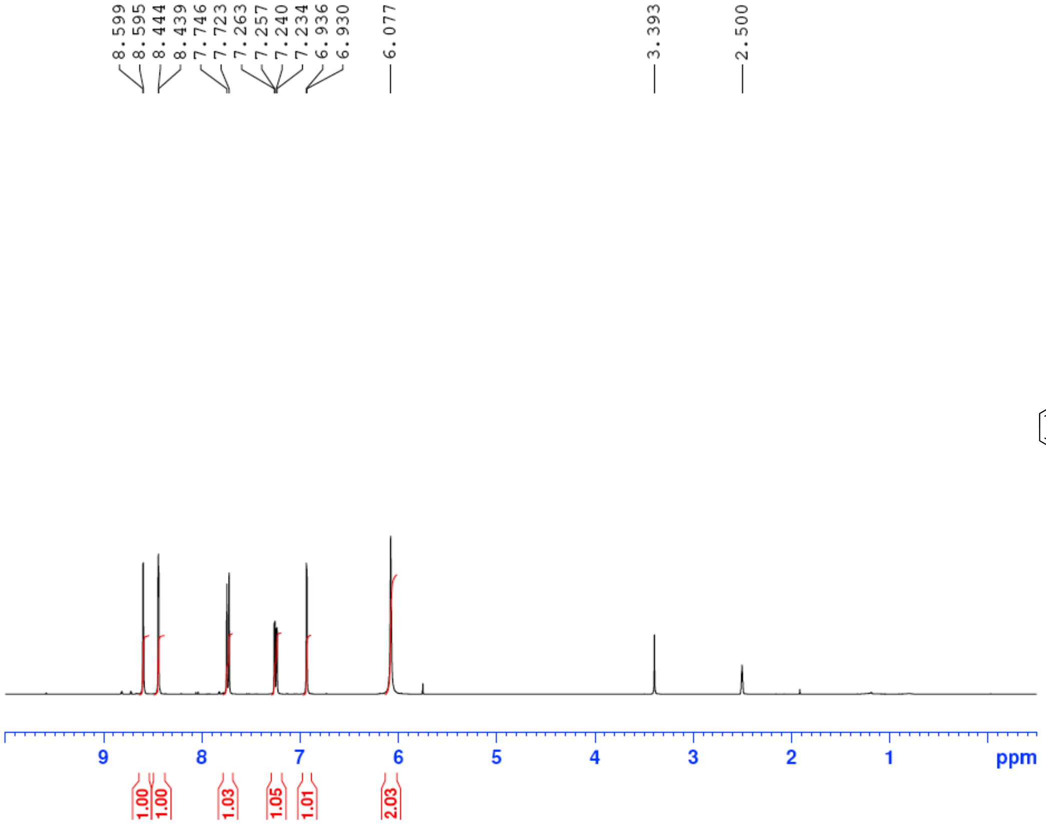




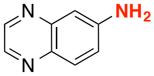
```
Current Data Parameters
NAME     CWO-V-170B-sep-3 (DMSO) (13C)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120922
Time                 3.33
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                  65536
SOLVENT              DMSO
NS                    109
DS                      2
SWH             23980.814 Hz
FIDRES           0.365919 Hz
AQ              1.3664756 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  297.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6128139 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

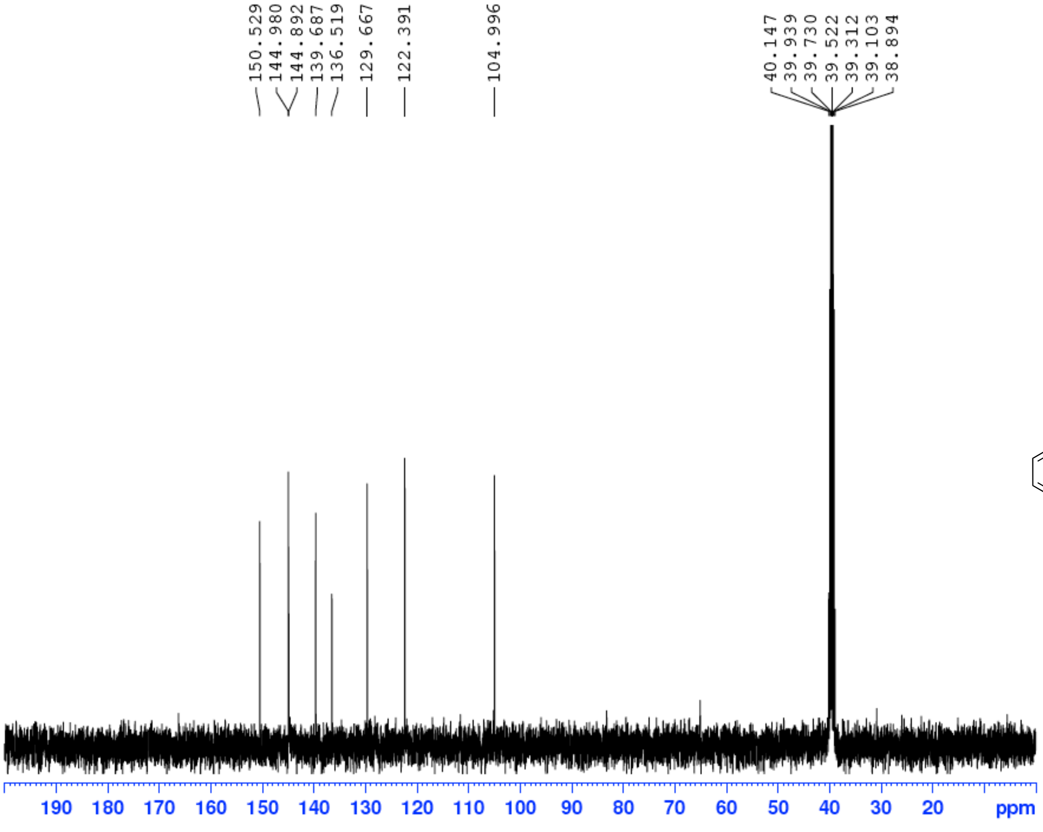


^{1}H and ^{13}C NMR of 6-Aminoquinoxaline (**5p**)

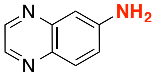


```
Current Data Parameters
NAME     CWC-V-267A-sep (H1)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121104
Time                   0.58
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       18
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                     35.9
DW                   60.400 usec
DE                     6.00 usec
TE                    298.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.07 usec
PL1      0 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF              400.1300027 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

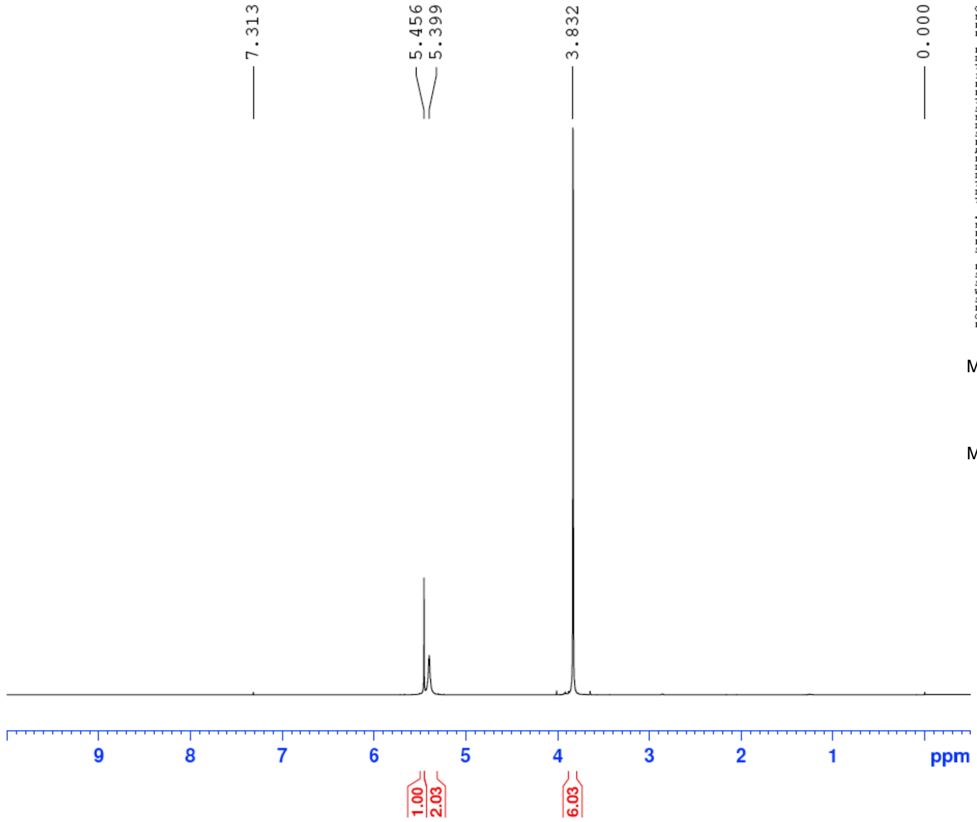




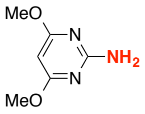
```
Current Data Parameters
NAME     CWC-V-267A-sep (C13)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121104
Time                   1.03
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT                DMSO
NS                       55
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664256 sec
RG                  18390.4
DW                   20.850 usec
DE                     6.00 usec
TE                    298.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1
SFO1            100.6228298 MHz
NUC1                    13C
P1                     8.75 usec
PLW1            -1.00000000 W
SFO2            400.1316005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 90.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W
PLW13           -1.00000000 W

F2 - Processing parameters
SI                    65536
SF              100.6128155 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

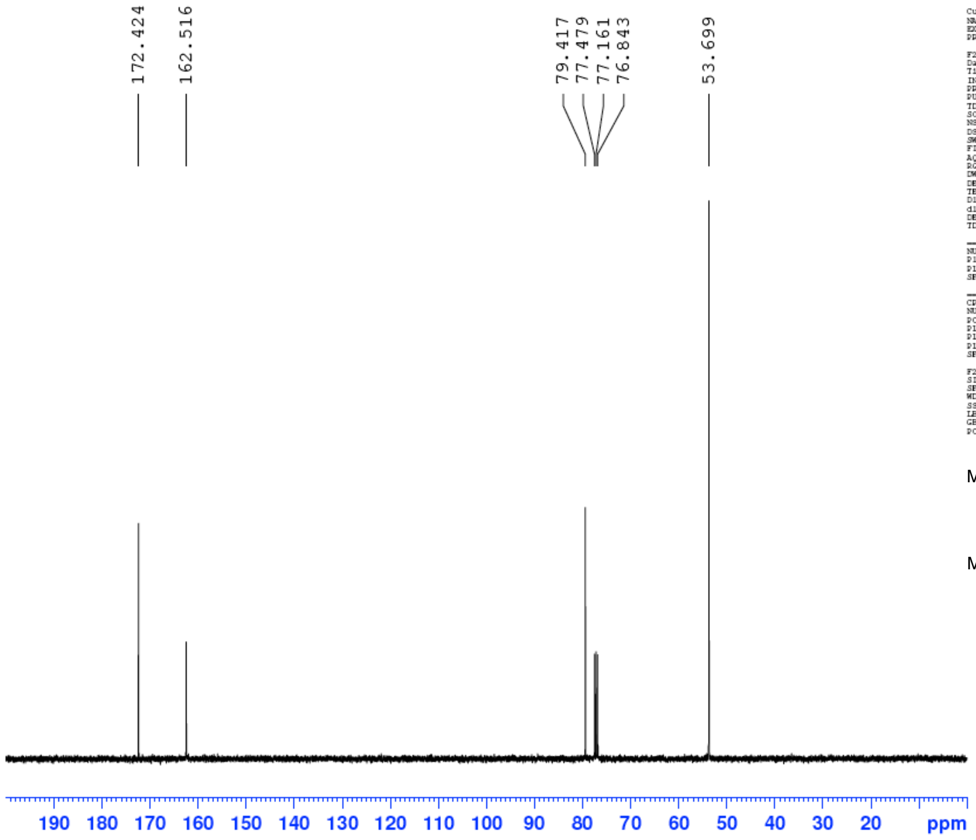


^{1}H and ^{13}C NMR of 2-Amino-4,6-dimethoxypyrimidine (**5q**)

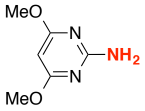


```
Current Data Parameters
NAME      CWC-V-171A-sep (1H)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120913
Time                 19.16
INSTRUM              spect
PROBHD     5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      15
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                    35.9
DW                  60.400 usec
DE                    6.00 usec
TE                   297.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1                   0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1299887 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

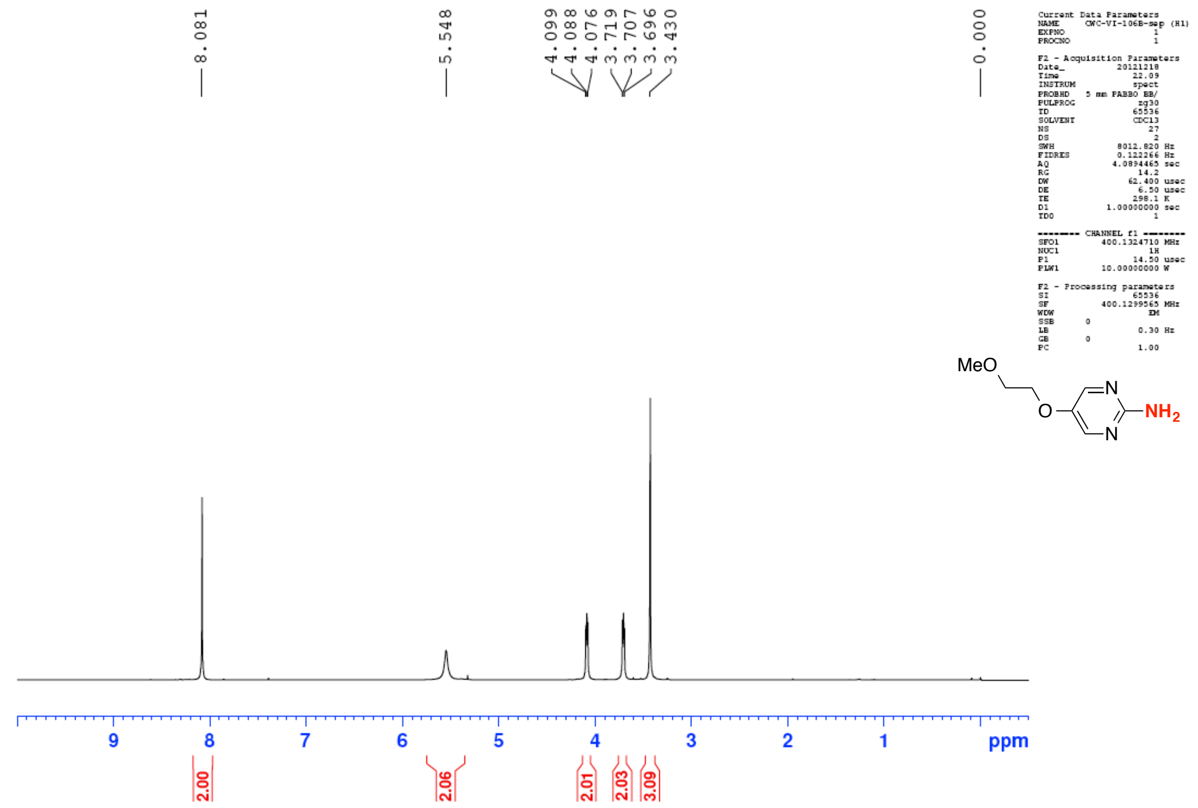




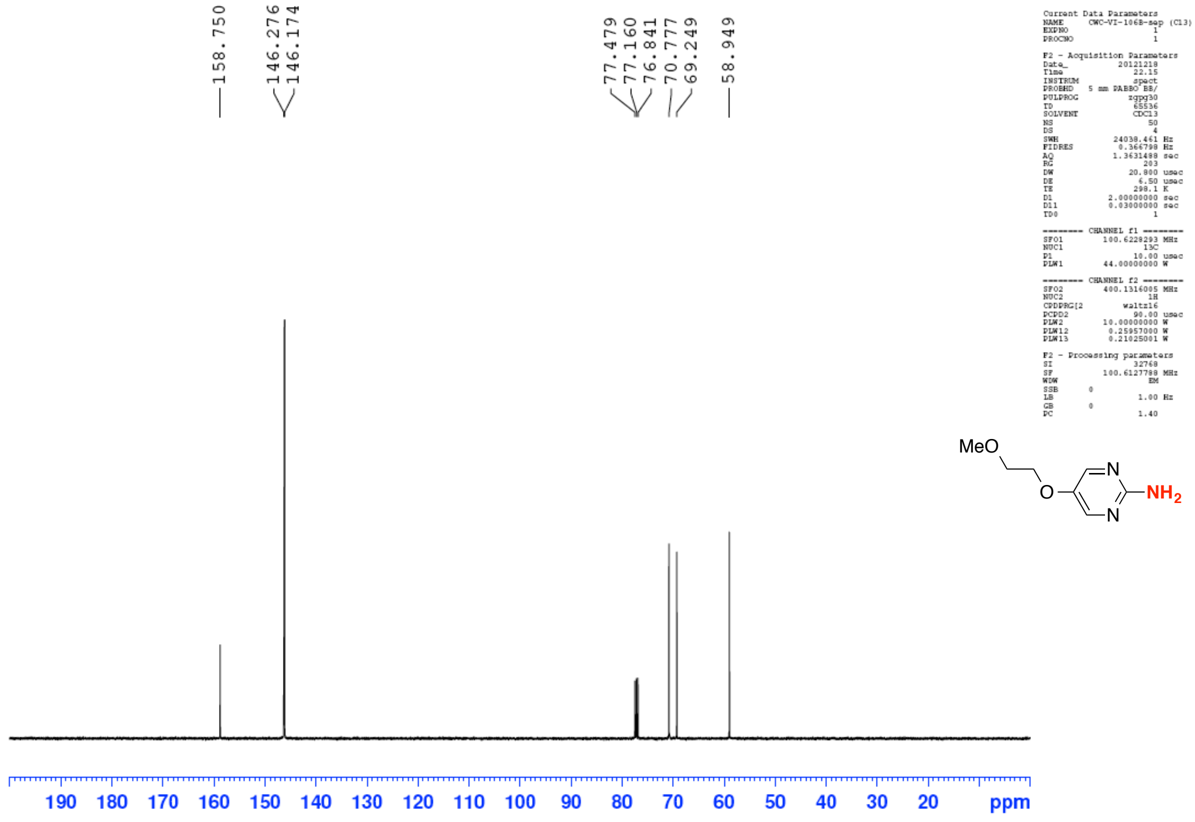
```
Current Data Parameters
NAME      CWC-V-171A-sep (13C)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120913
Time                 19.19
INSTRUM              spect
PROBHD     5 mm BBO BB-1H
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      33
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664756 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.75 usec
PL1                  -3.00 dB
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 14.52 dB
PL13                 18.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
SI                   65536
SF             100.6127662 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



^{1}H and ^{13}C NMR of 2-Amino-5-(2-methoxyethoxy)pyrimidine (**5r**)

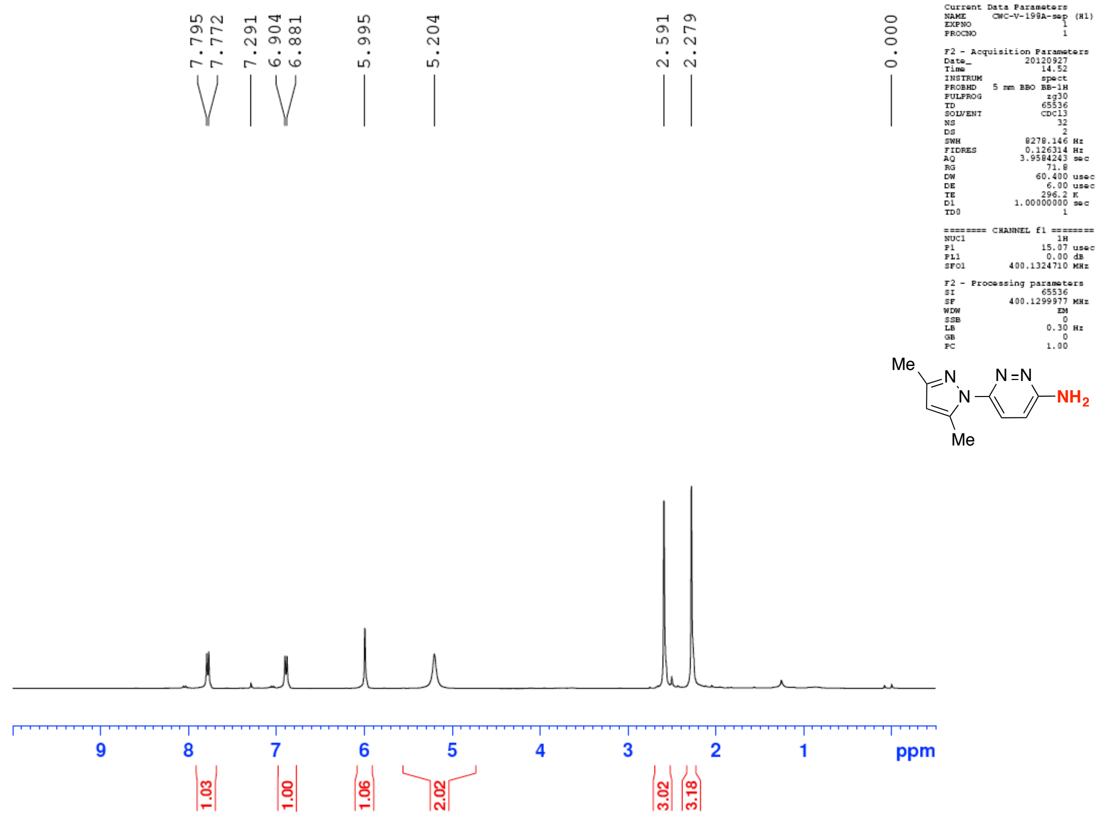


```
Current Data Parameters
NAME     CWC-VI-106B-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121218
Time                22.09
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     27
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                   14.2
DW                 62.400 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.1324710 MHz
NUC1                   1H
P1                  14.50 usec
PLW1          10.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.1299565 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

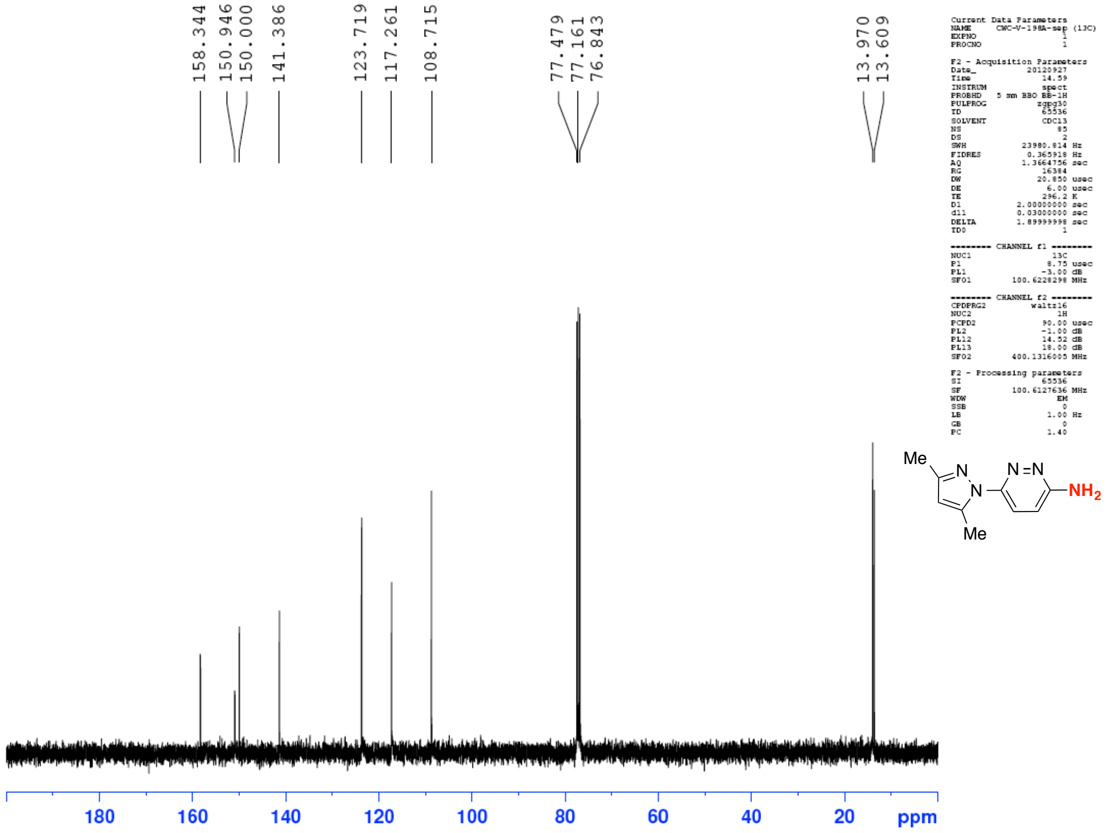


```
Current Data Parameters
NAME     CWC-VI-106B-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121218
Time                22.15
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     50
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631488 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          100.6228293 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          44.00000000 W

======== CHANNEL f2 ========
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          10.00000000 W
PLW12          0.25957000 W
PLW13          0.21025001 W

F2 - Processing parameters
SI                  32768
SF            100.6127788 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

^{1}H and ^{13}C NMR of 3-Amino-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine (**5s**)

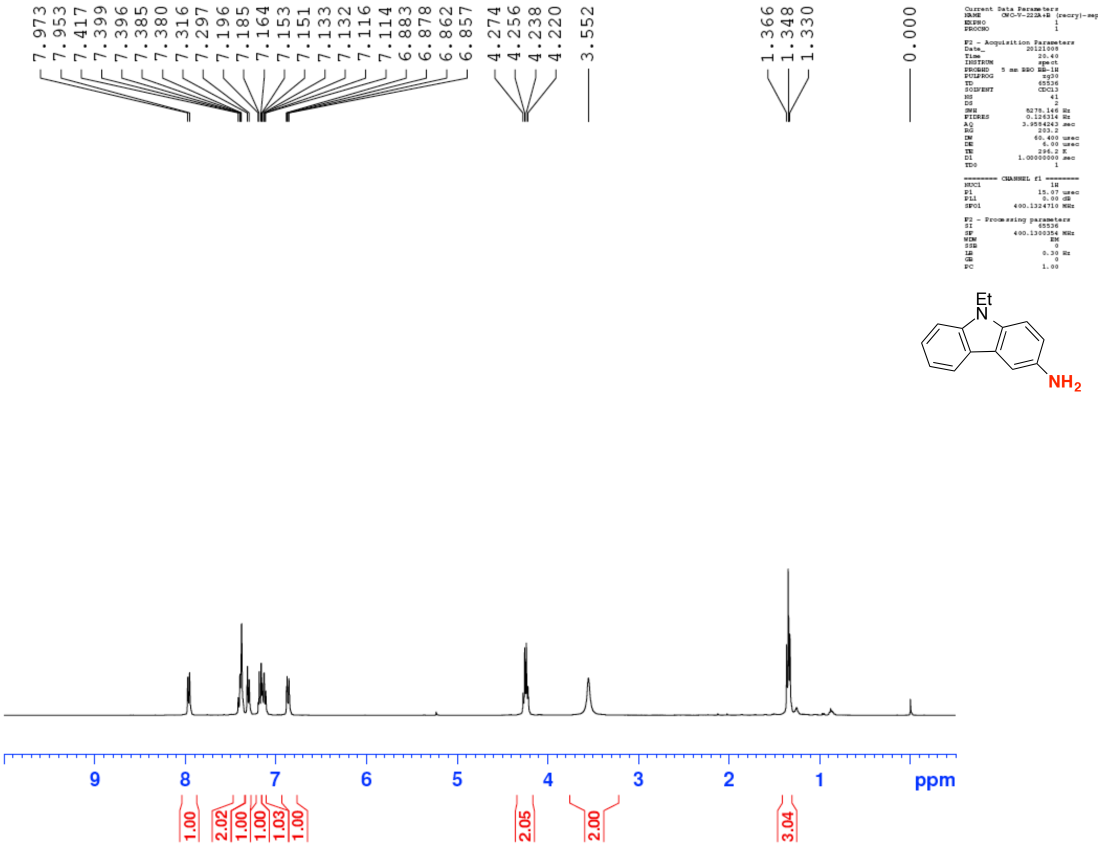


```
Current Data Parameters
NAME     CWC-V-198A-sep (H1)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120927
Time                  14.52
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9584243 sec
RG                     71.8
DW                   60.400 usec
DE                     6.00 usec
TE                    296.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.07 usec
PL1                    0.00 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF              400.1299977 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

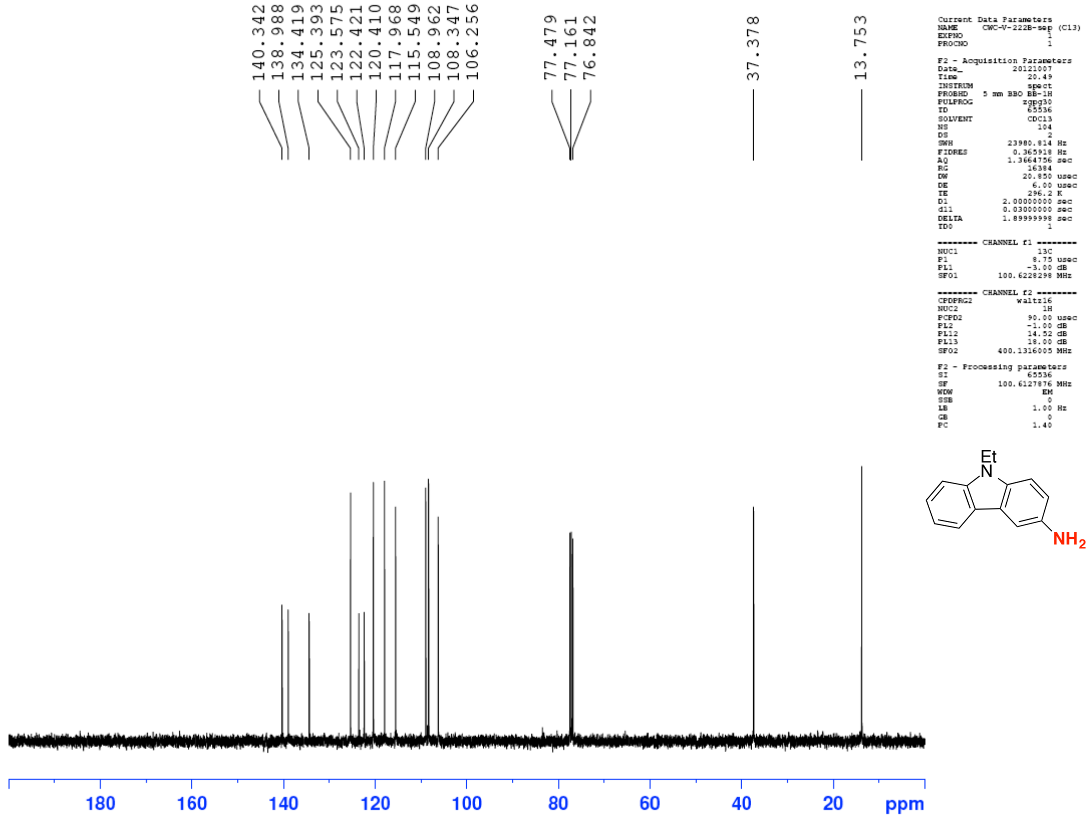


```
Current Data Parameters
NAME     CWC-V-198A-sep (13C)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20120927
Time                  14.59
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       85
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                    16384
DW                   20.850 usec
DE                     6.00 usec
TE                    296.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.75 usec
PL1                   -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -1.00 dB
PL12                  14.52 dB
PL13                  18.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    65536
SF              100.6127636 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{1}H and ^{13}C NMR of 3-Amino-9-ethyl-9*H*-carbazole (**5t**)

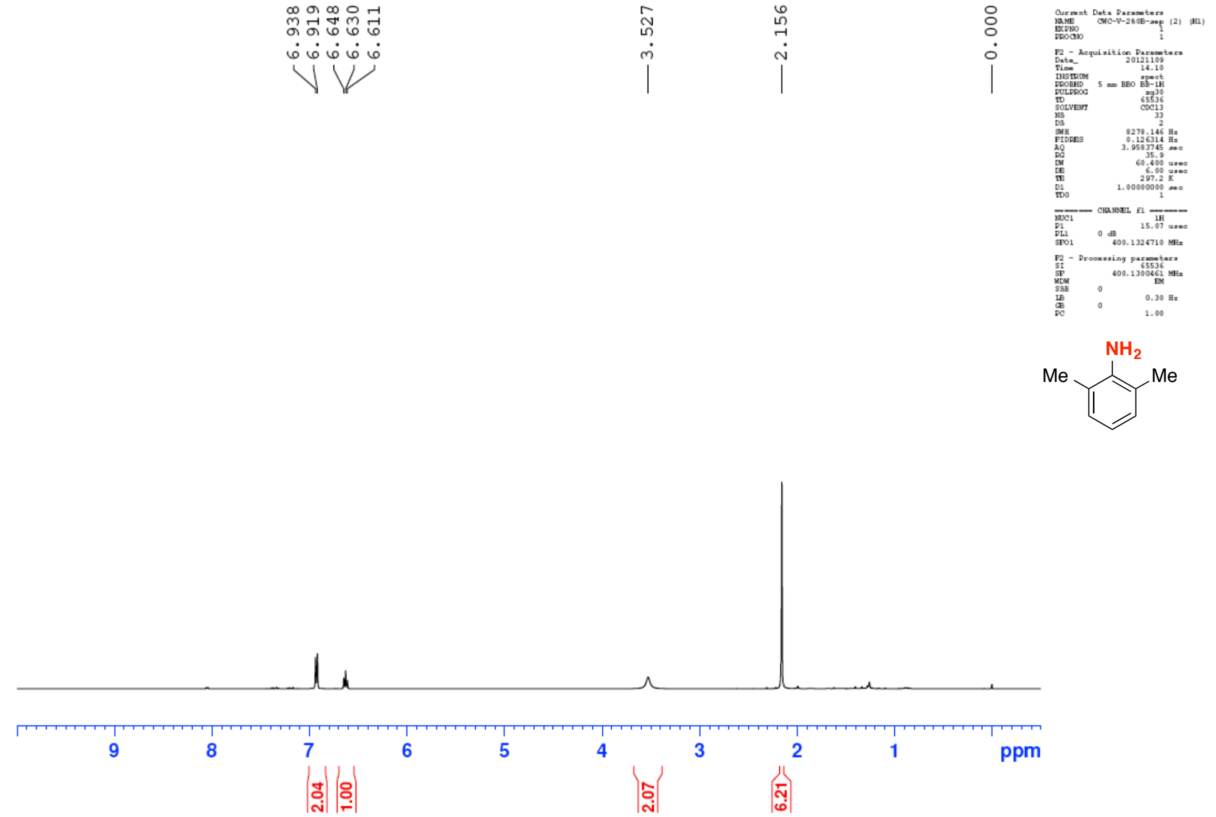


```
Current Data Parameters
NAME     CWC-V-222A+B (recry)-sep
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121008
Time                20.40
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     41
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  203.2
DW                 60.400 usec
DE                   6.00 usec
TE                  296.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300354 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

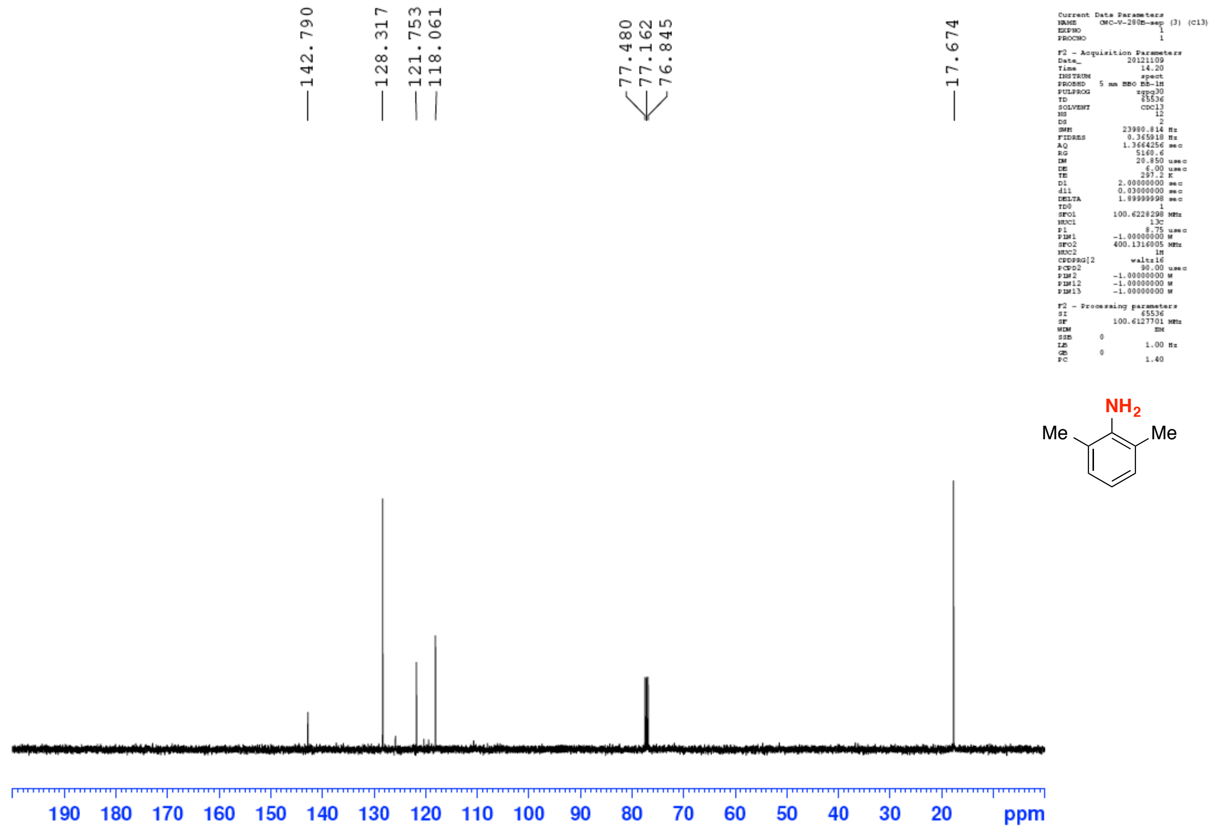


```
Current Data Parameters
NAME     CWC-V-222B-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121007
Time                20.49
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    104
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664756 sec
RG                  16384
DW                 20.850 usec
DE                   6.00 usec
TE                  296.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               90.00 usec
PL2                 -1.00 dB
PL12                14.52 dB
PL13                18.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  65536
SF            100.6127876 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{1}H and ^{13}C NMR of 2,6-Dimethylaniline (**6a**)

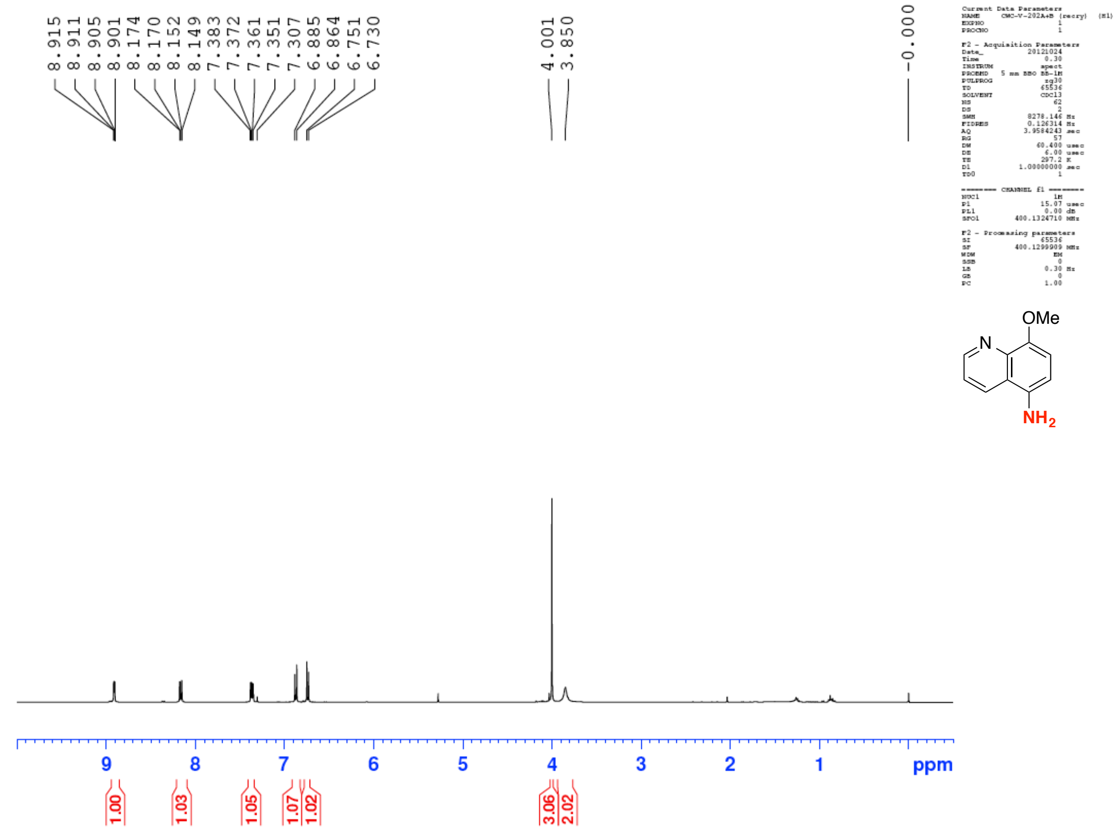


```
Current Data Parameters
NAME      CMC-V-280B-sep (2) (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121109
Time               14.10
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    33
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9583745 sec
RG                  35.9
DW                60.400 usec
DE                  6.00 usec
TE                 297.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.07 usec
PL1      0 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300461 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

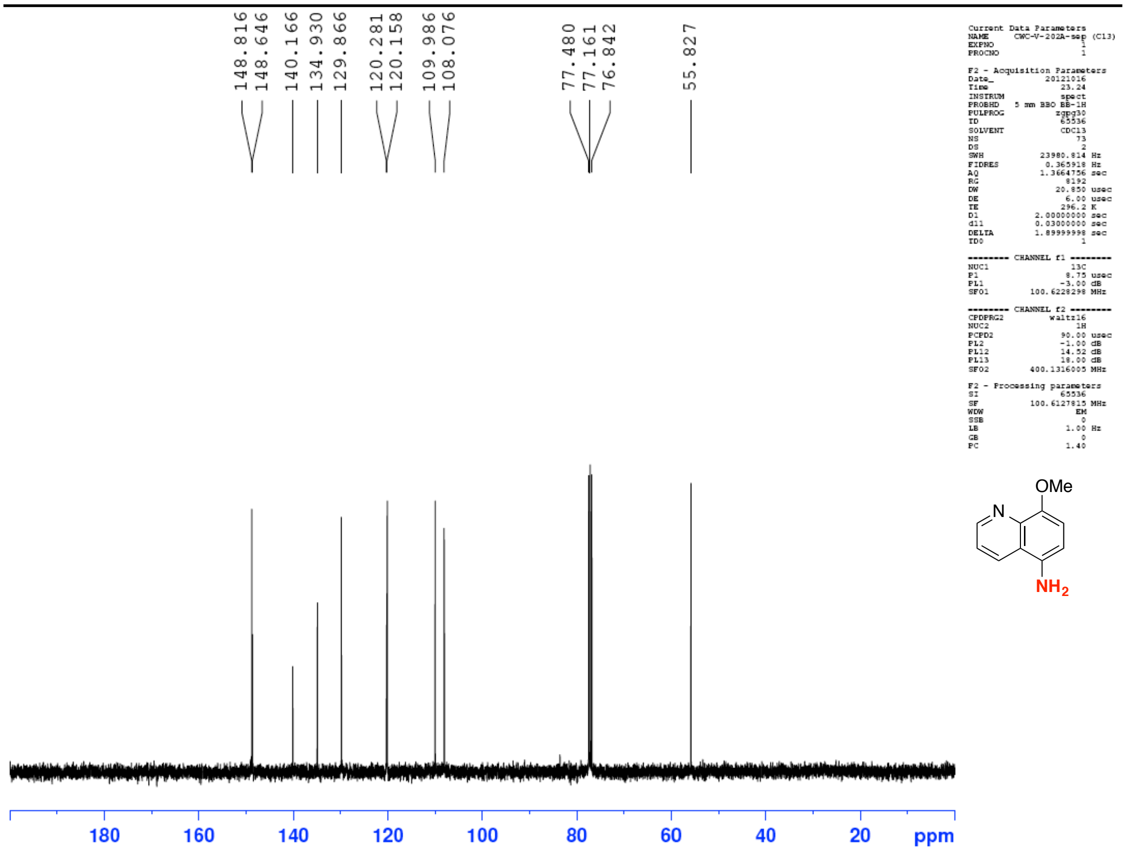


```
Current Data Parameters
NAME      CMC-V-280B-sep (3) (C13)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121109
Time               14.20
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    12
DS                     2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664256 sec
RG                5160.6
DW                20.850 usec
DE                  6.00 usec
TE                 297.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1
SFO1         100.6228298 MHz
NUC1                 13C
P1                  8.75 usec
PLW1         -1.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         -1.00000000 W
PLW12        -1.00000000 W
PLW13        -1.00000000 W

F2 - Processing parameters
SI                 65536
SF           100.6127701 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

^{1}H and ^{13}C NMR of 5-Amino-8-methoxyquinoline (**6b**)

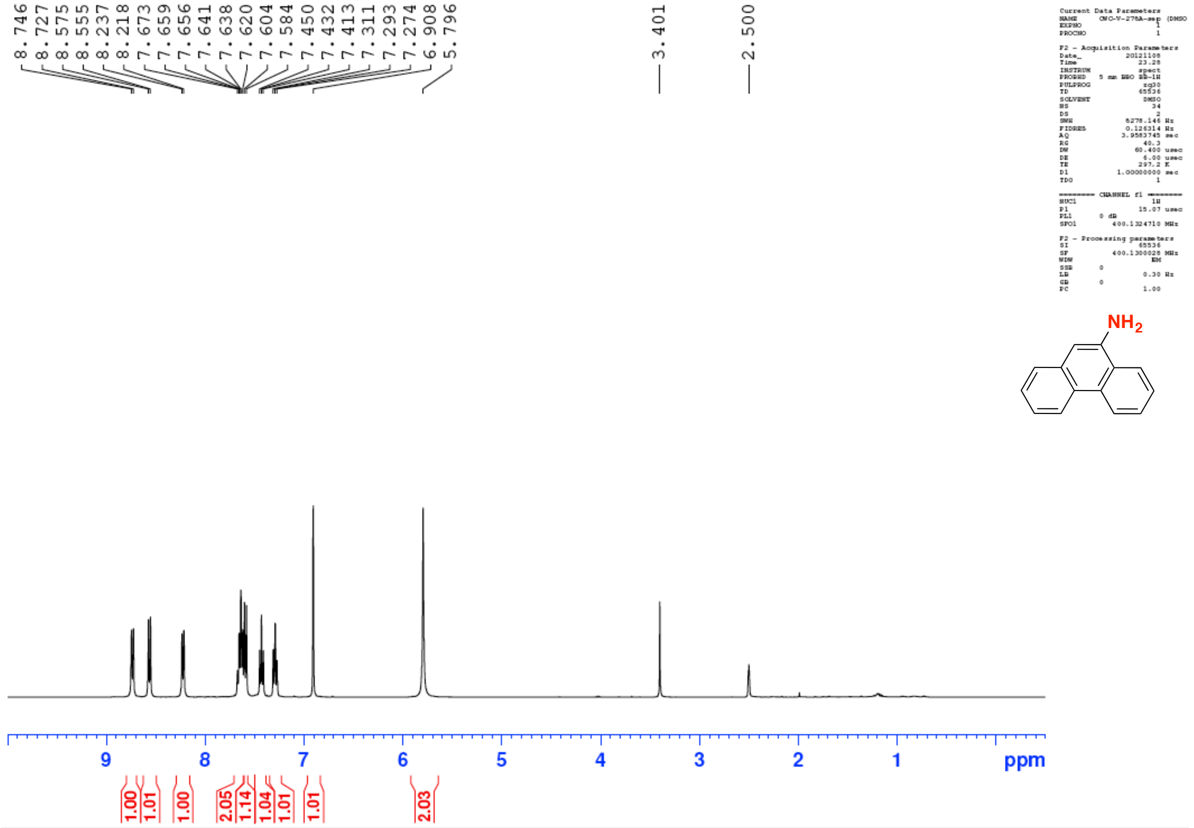


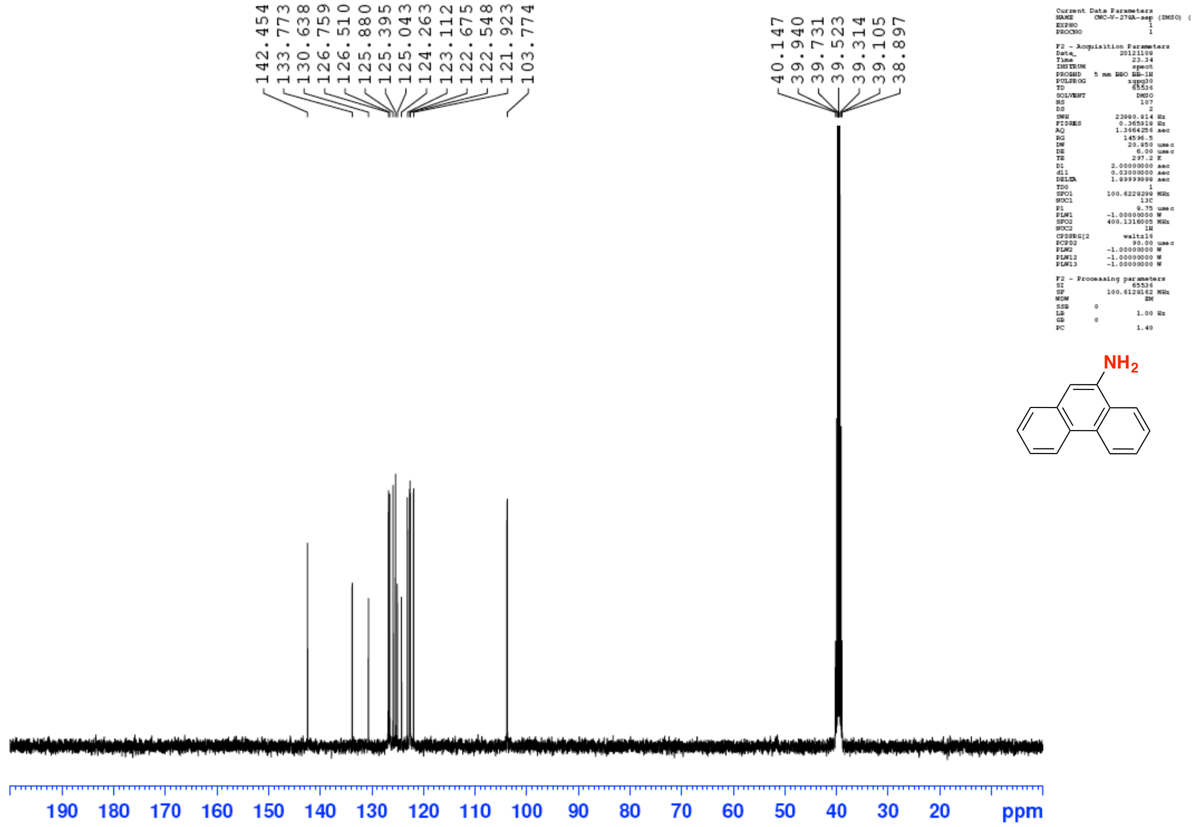
```
Current Data Parameters
NAME      CWC-V-202A+B (recry)   (H1)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121024
Time                   0.30
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       62
DS                        2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                       57
DW               60.400 usec
DE                 6.00 usec
TE                  297.2 K
D1           1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                15.07 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF          400.1299909 MHz
WDW                      EM
SSB                       0
LB                  0.30 Hz
GB                        0
PC                     1.00
```



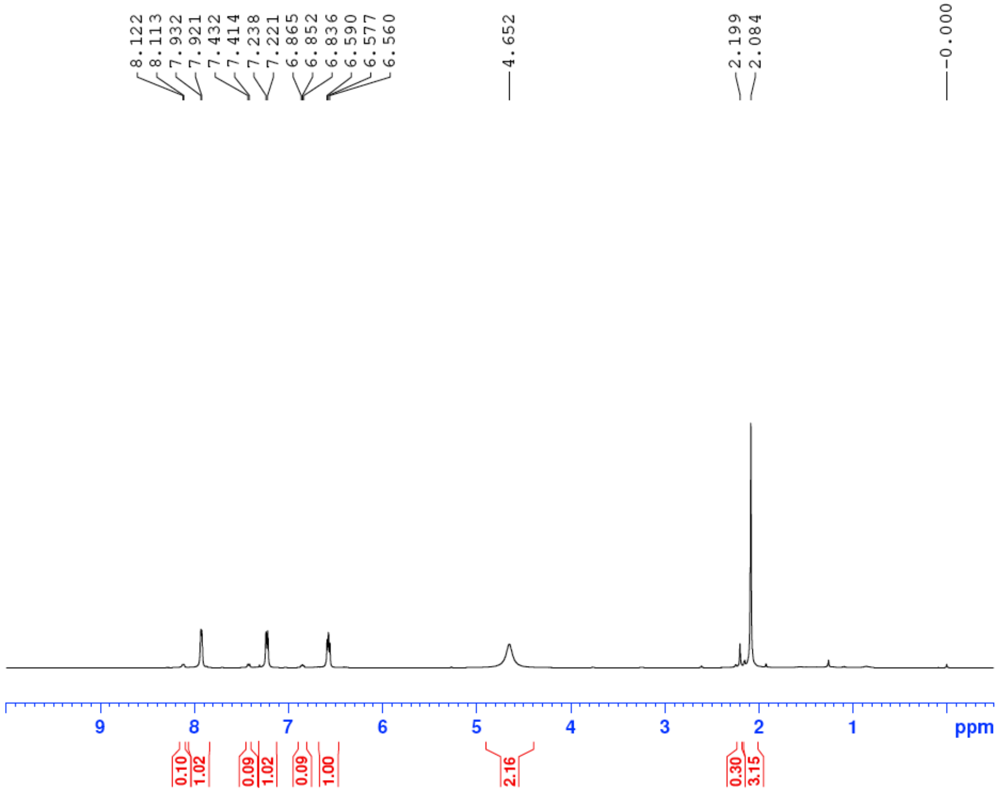
```
Current Data Parameters
NAME      CWC-V-202A-sep (C13)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121016
Time                  23.24
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       73
DS                        2
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG                     8192
DW               20.850 usec
DE                 6.00 usec
TE                  296.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                 8.75 usec
PL1               -3.00 dB
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              14.52 dB
PL13              18.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                    65536
SF          100.6127815 MHz
WDW                      EM
SSB                       0
LB                  1.00 Hz
GB                        0
PC                     1.40
```

^{1}H and ^{13}C NMR of 9-Aminphenanthrene (**6c**)

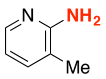


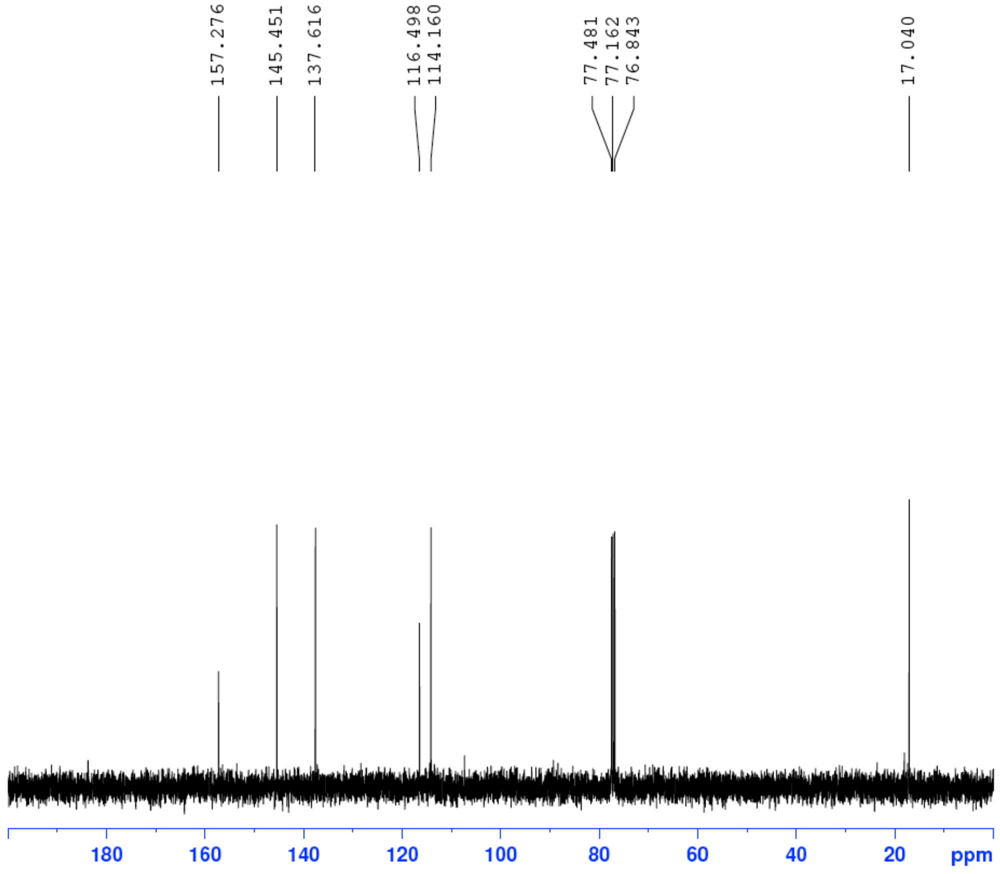


^{1}H and ^{13}C NMR of 2-Amino-3-methylpyridine (**6d**)

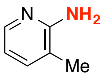


```
Current Data Parameters
NAME       CWC-V-234A-sep (H1)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121023
Time                  23.52
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       36
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                3.9583745 sec
RG                       32
DW                   60.400 usec
DE                     6.00 usec
TE                    297.2 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.07 usec
PL1        0 dB
SFO1            400.1324710 MHz

F2 - Processing parameters
SI                    65536
SF              400.1299904 MHz
WDW                      EM
SSB        0
LB                     0.30 Hz
GB         0
PC                     1.00
```

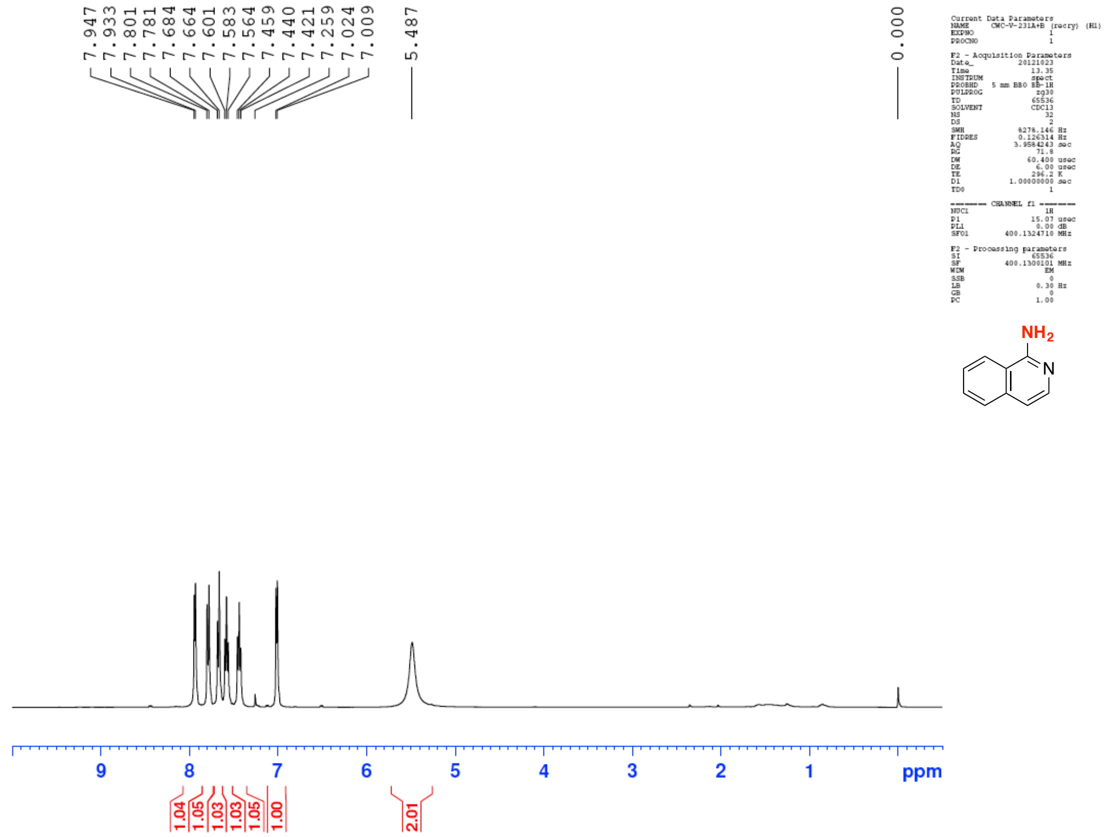


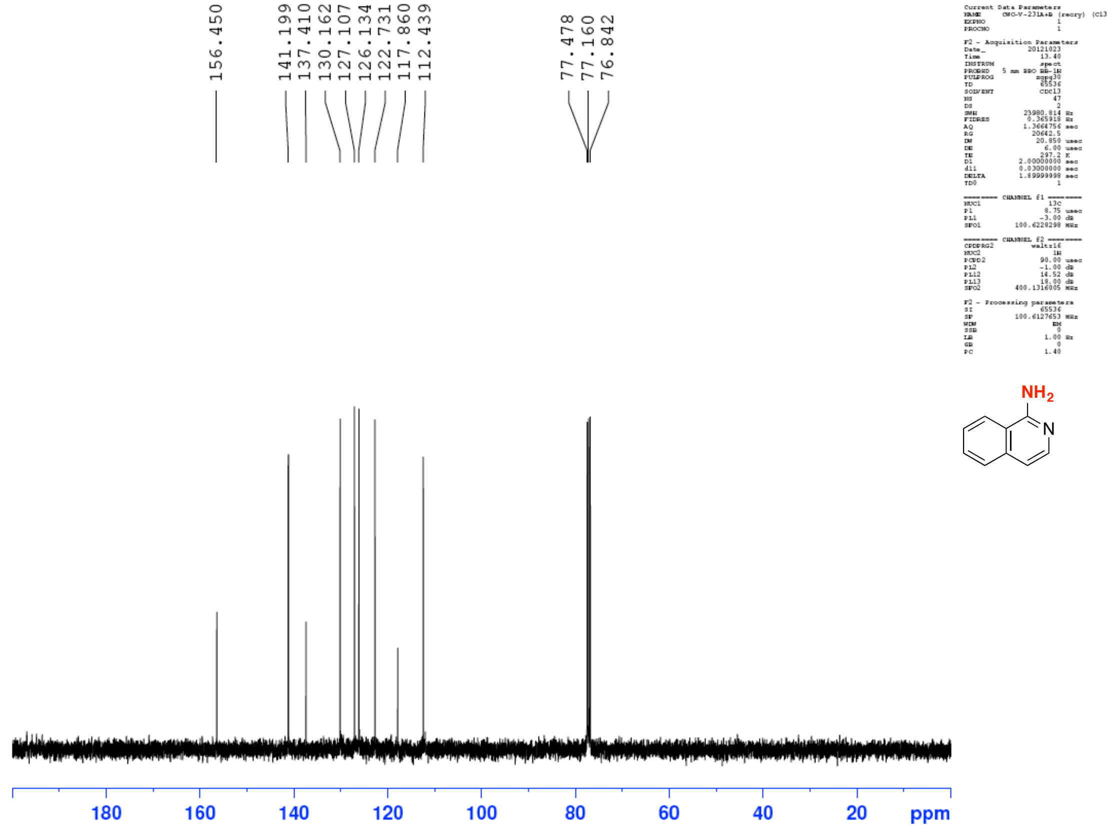


```
Current Data Parameters
NAME       CWC-V-234A-sep (C13)
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20121024
Time                   0.00
INSTRUM               spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       39
DS                        2
SWH               23980.814 Hz
FIDRES             0.365918 Hz
AQ                1.3664756 sec
RG                     8192
DW                   20.850 usec
DE                     6.00 usec
TE                    297.2 K
D1               2.00000000 sec
d11              0.03000000 sec
DELTA            1.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.75 usec
PL1                   -3.00 dB
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -1.00 dB
PL12                  14.52 dB
PL13                  18.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                    65536
SF              100.6127739 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

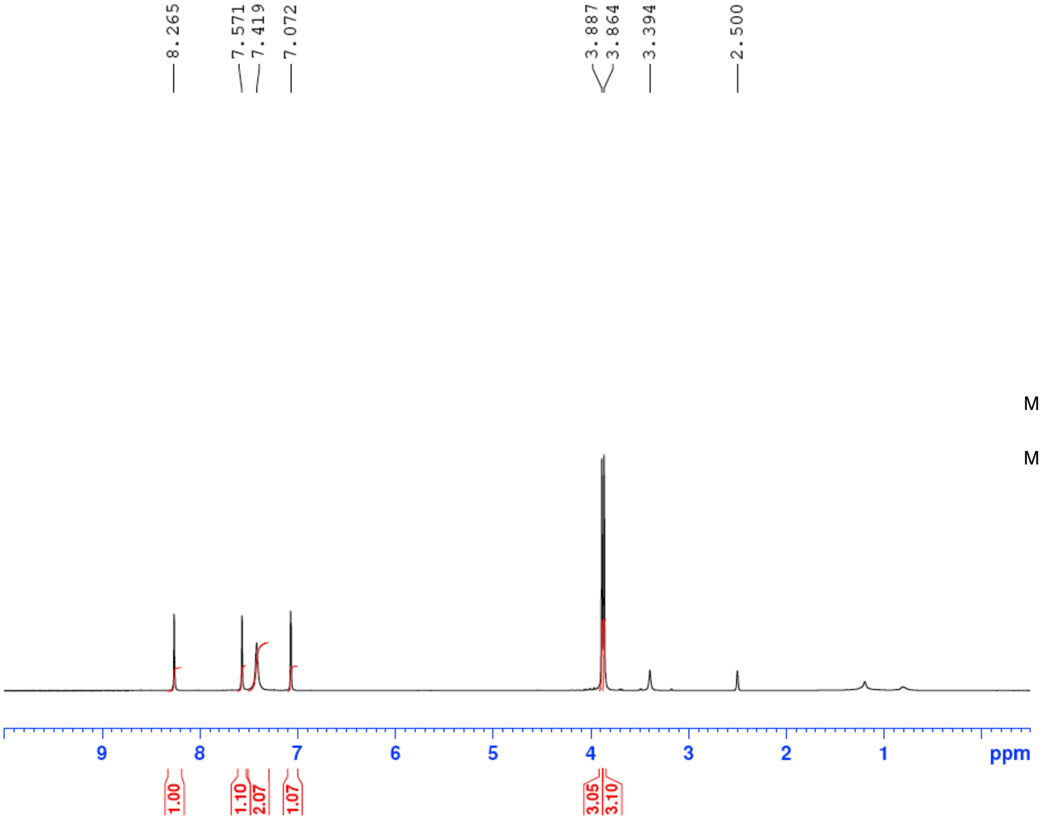


^{1}H and ^{13}C NMR of 1-Aminoisoquinoline (**6e**)

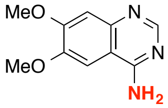


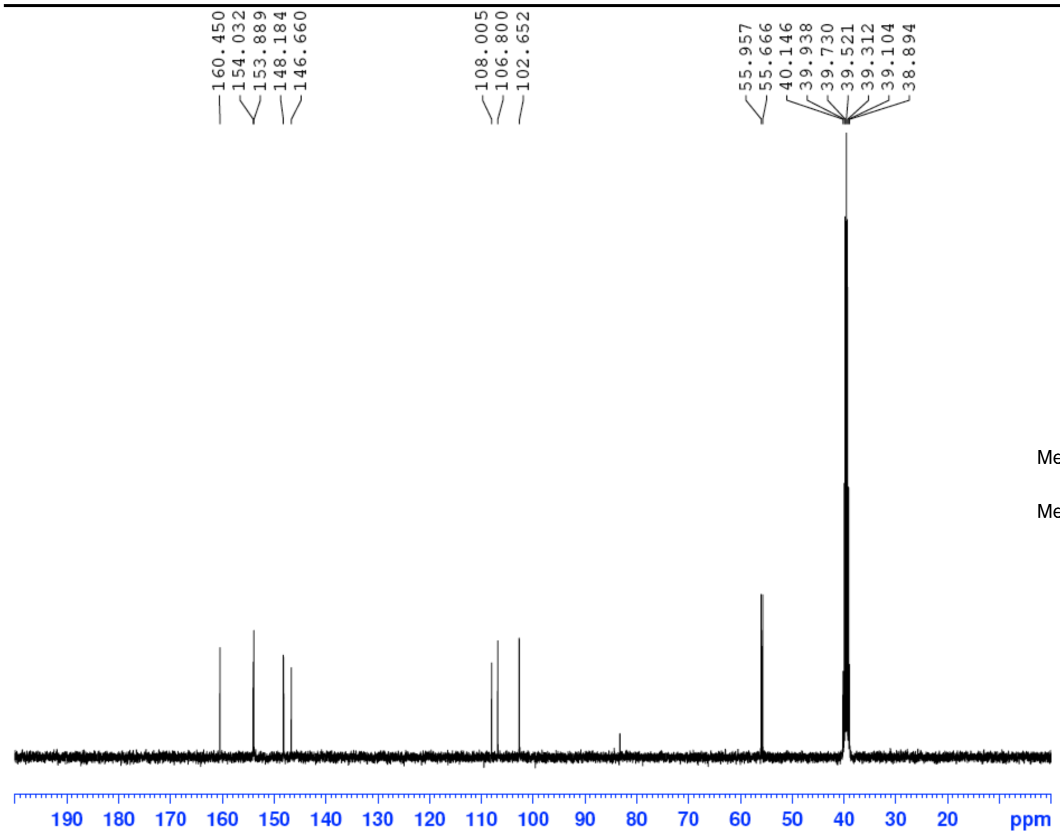


^{1}H and ^{13}C NMR of 4-Amino-6,7-dimethoxyquinazoline (**6f**)

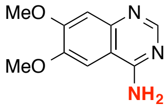


```
Current Data Parameters
NAME       CWC-V-270A-sep (H1)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121031
Time                 15.28
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      15
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9583745 sec
RG                    90.5
DW                  60.400 usec
DE                    6.00 usec
TE                   297.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.07 usec
PL1       0 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                   65536
SF             400.1300037 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```

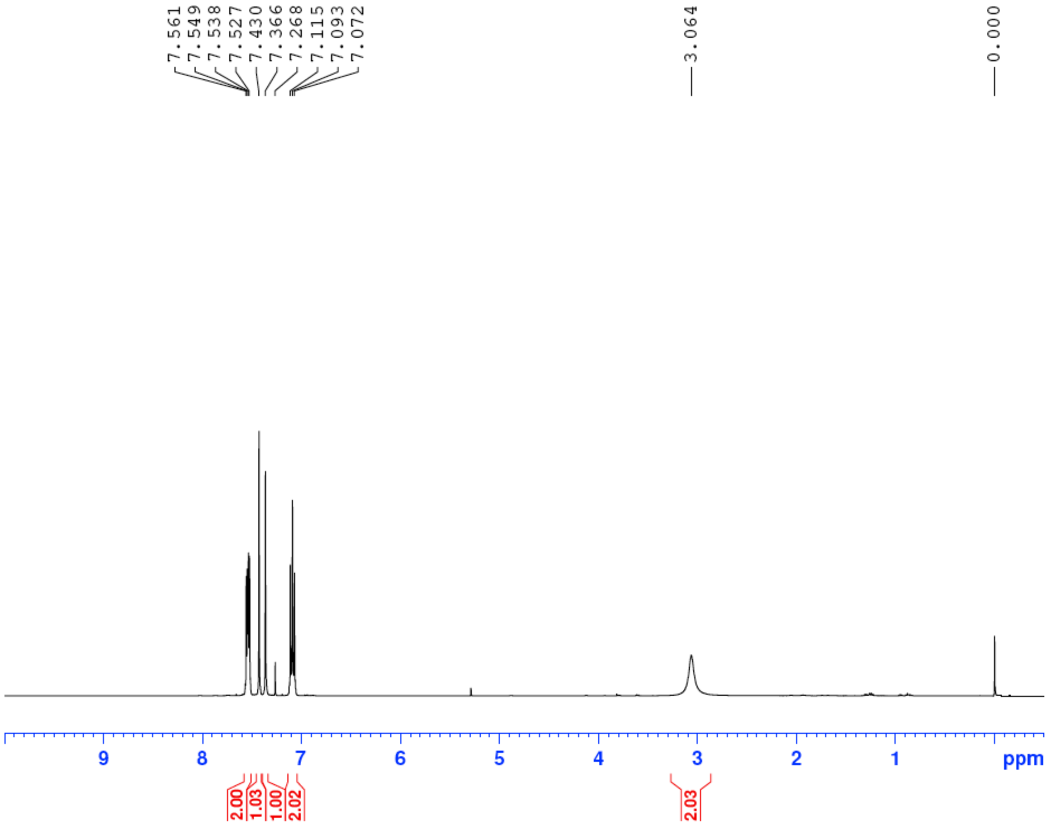




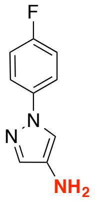
```
Current Data Parameters
NAME       CWC-V-270A-sep (C13)
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121031
Time                 15.31
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   65536
SOLVENT               DMSO
NS                     162
DS                       2
SWH              23980.814 Hz
FIDRES            0.365918 Hz
AQ               1.3664256 sec
RG                   16384
DW                  20.850 usec
DE                    6.00 usec
TE                   297.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
TD0                      1
SFO1           100.6228298 MHz
NUC1                   13C
P1                    8.75 usec
PLW1           -1.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                   65536
SF             100.6128130 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

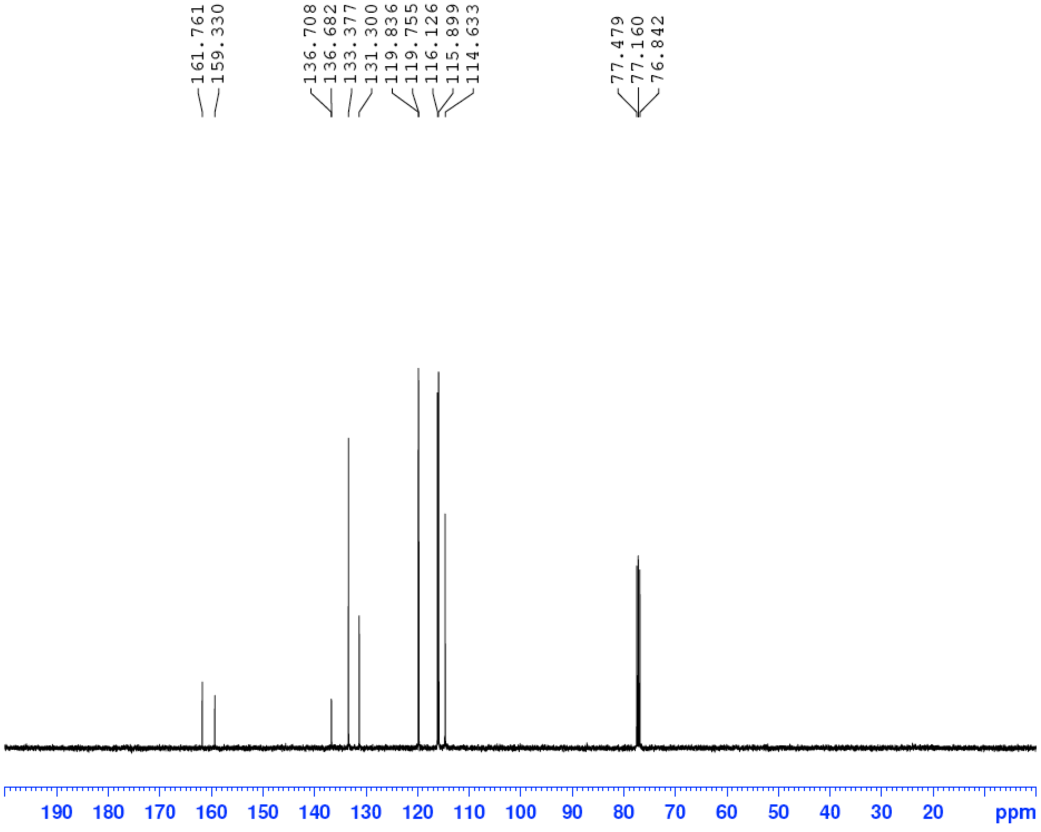


^1H and ^{13}C NMR of 4-Amino-1-(4-fluorophenyl)-1*H*-pyrazole (**7a**)

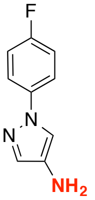


```
Current Data Parameters
NAME     CWC-VI-81A+B (recry) (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121213
Time               16.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    36
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                   128
DW                62.400 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 13.12 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300066 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

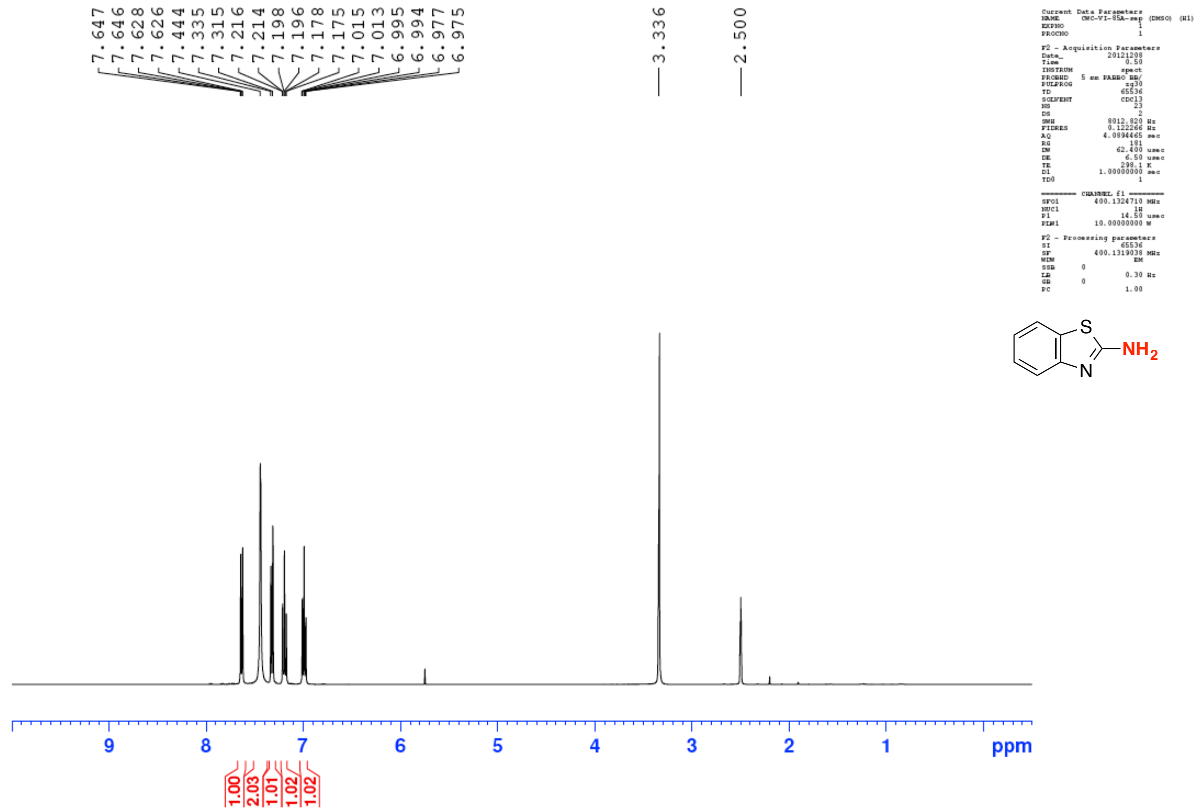


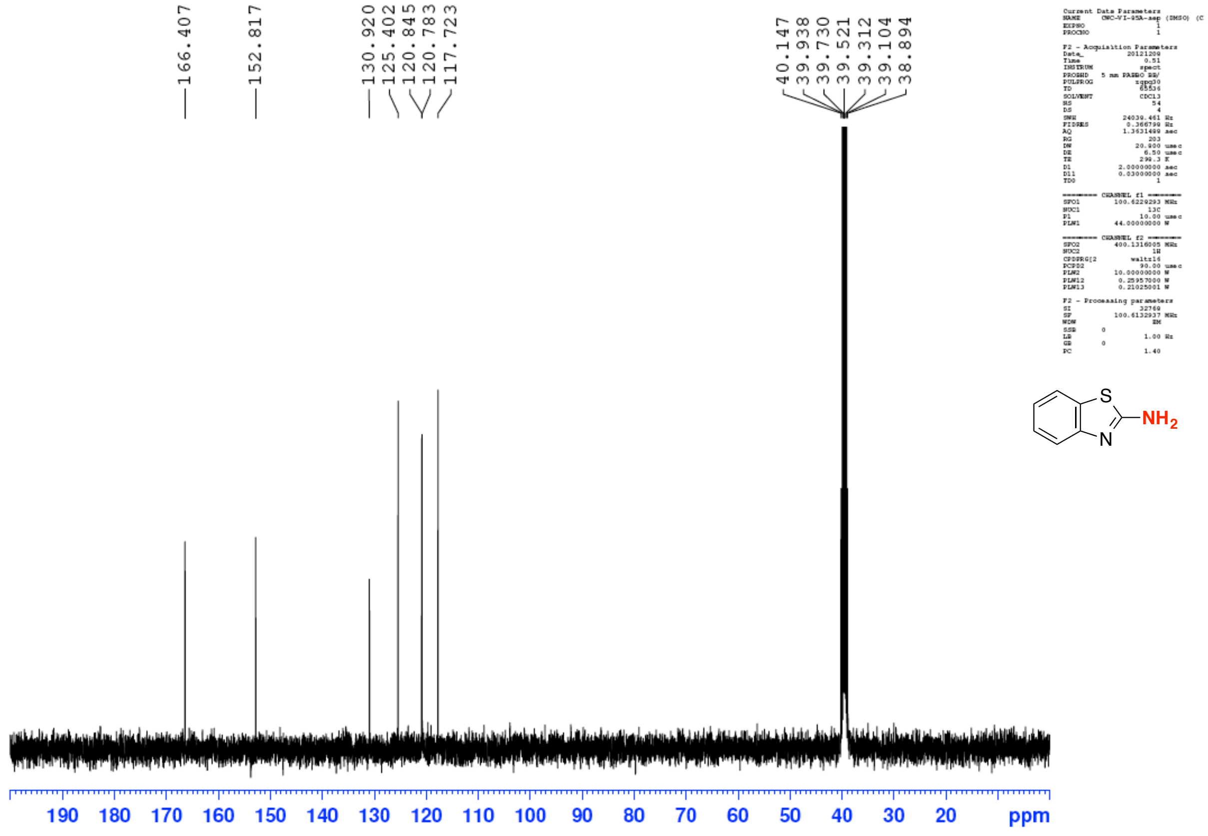


```
Current Data Parameters
NAME     CWC-VI-81A-sep (C13)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121208
Time                0.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    61
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         44.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         10.00000000 W
PLW12         0.25957000 W
PLW13         0.21025001 W

F2 - Processing parameters
SI                 32768
SF           100.6127710 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

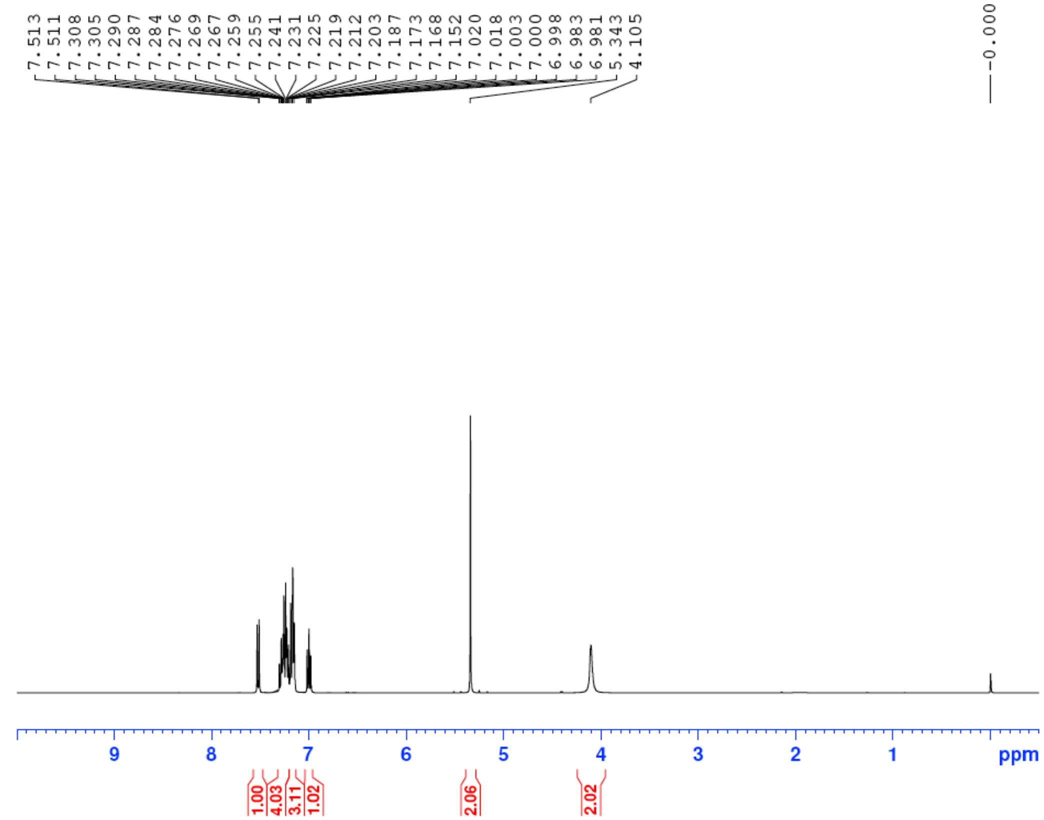


^{1}H and ^{13}C NMR of 2-Aminobenzothiazole (**7b**)

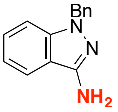


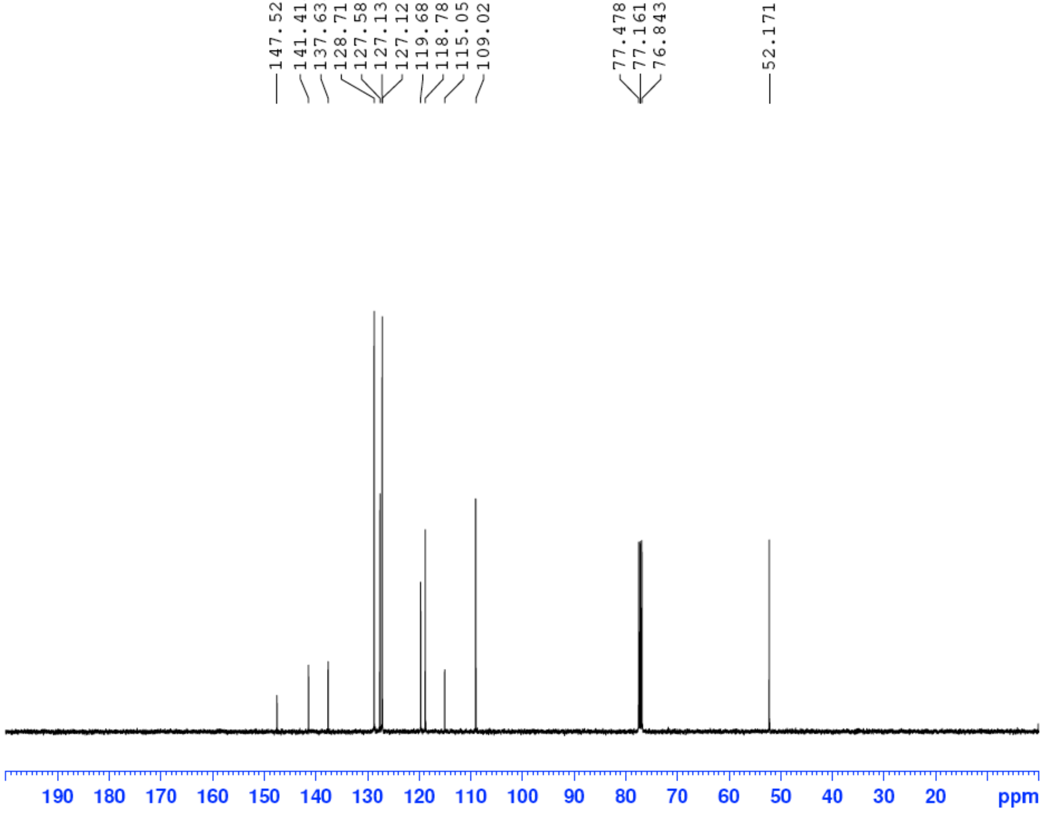


^{1}H and ^{13}C NMR of 3-Amino-1-benzyl-1*H*-indazole (**7c**)

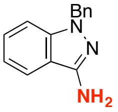


```
Current Data Parameters
NAME     CWC-VI-91A+B-sep (H1)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121211
Time               20.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    47
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                  80.6
DW                62.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 13.12 usec
PLW1         15.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300211 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

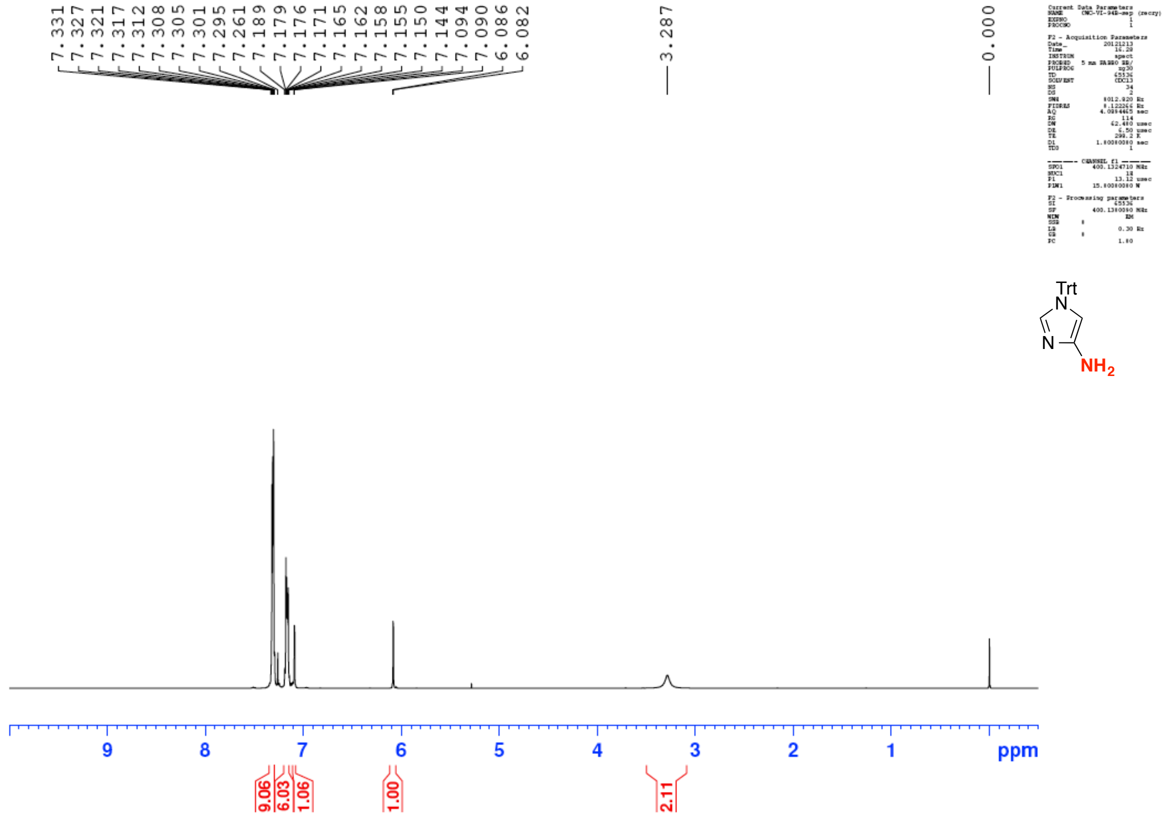


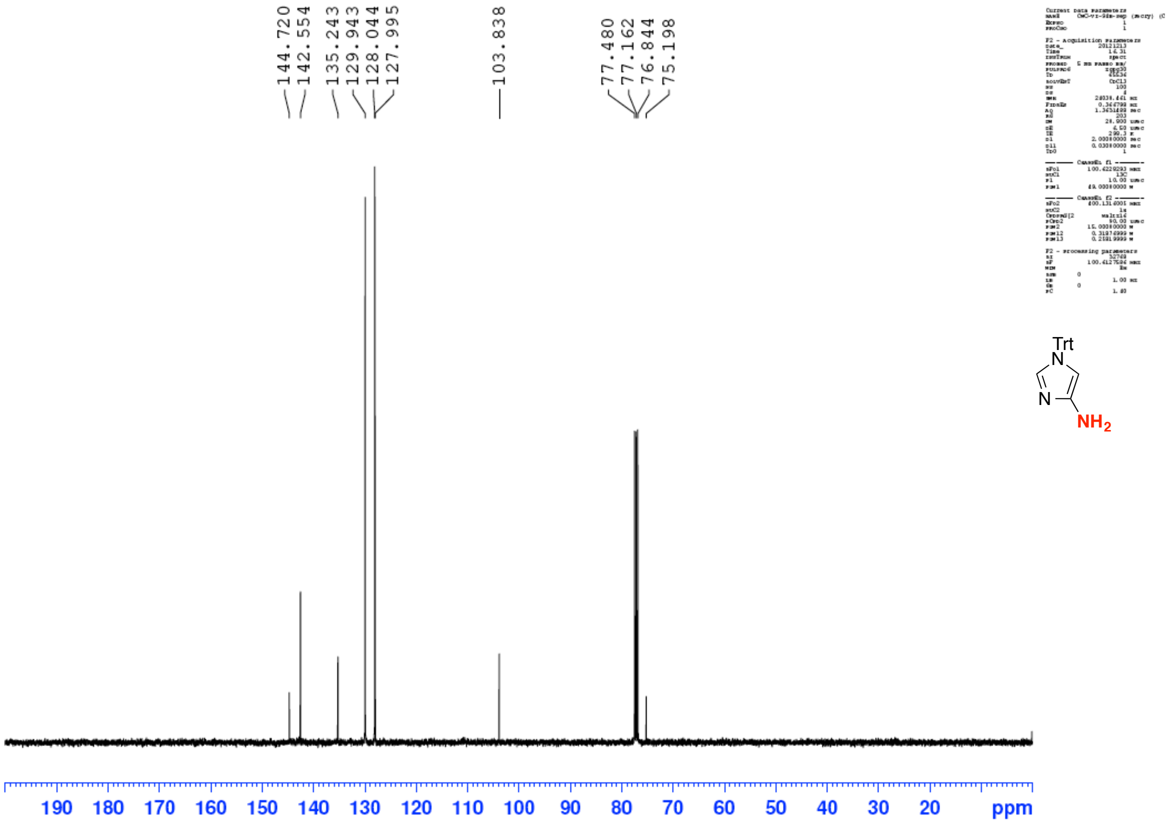


```
Current Data Parameters
NAME     CWC-VI-91A+B-sep (C13)
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121211
Time               20.45
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   235
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                   203
DW                20.800 usec
DE                  6.50 usec
TE                 298.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         49.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         15.00000000 W
PLW12         0.31876999 W
PLW13         0.25819999 W

F2 - Processing parameters
SI                 32768
SF           100.6127633 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

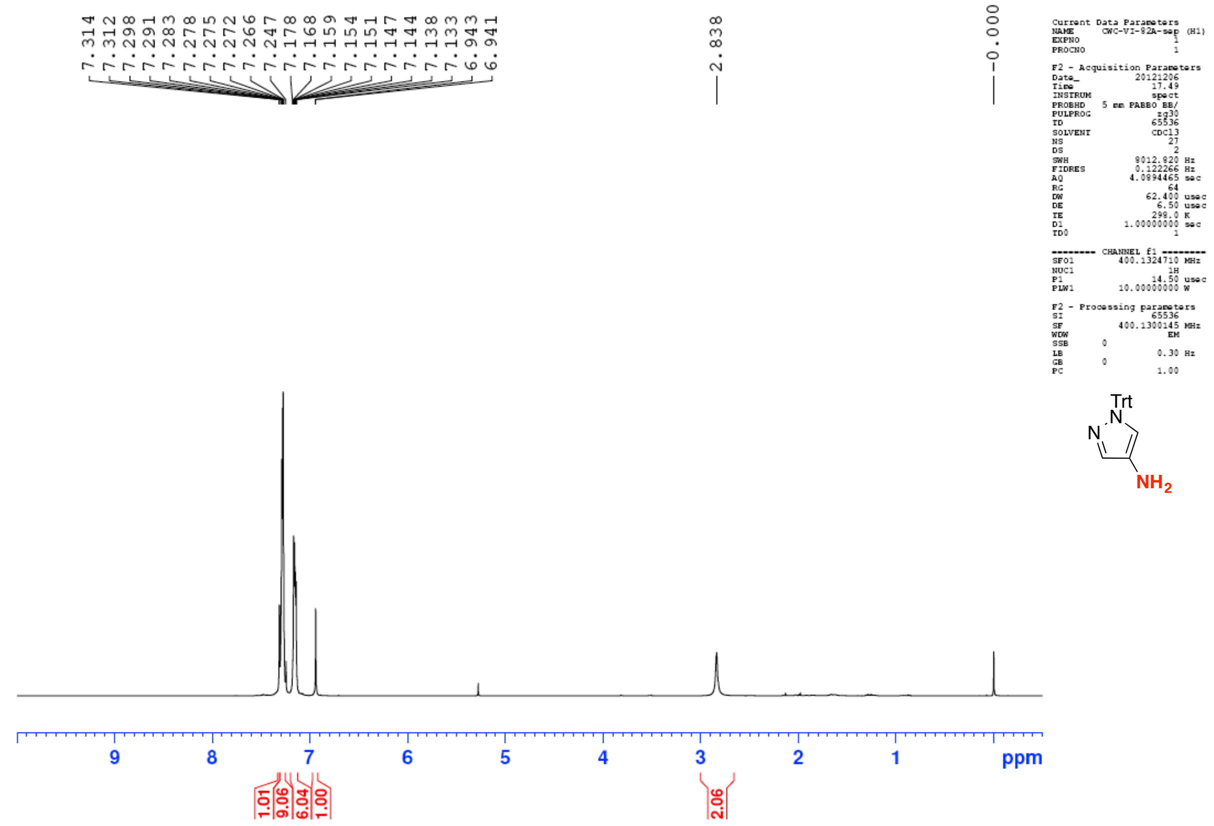


^{1}H and ^{13}C NMR of 4-Amino-1-trityl-1*H*-imidazole (**7d**)

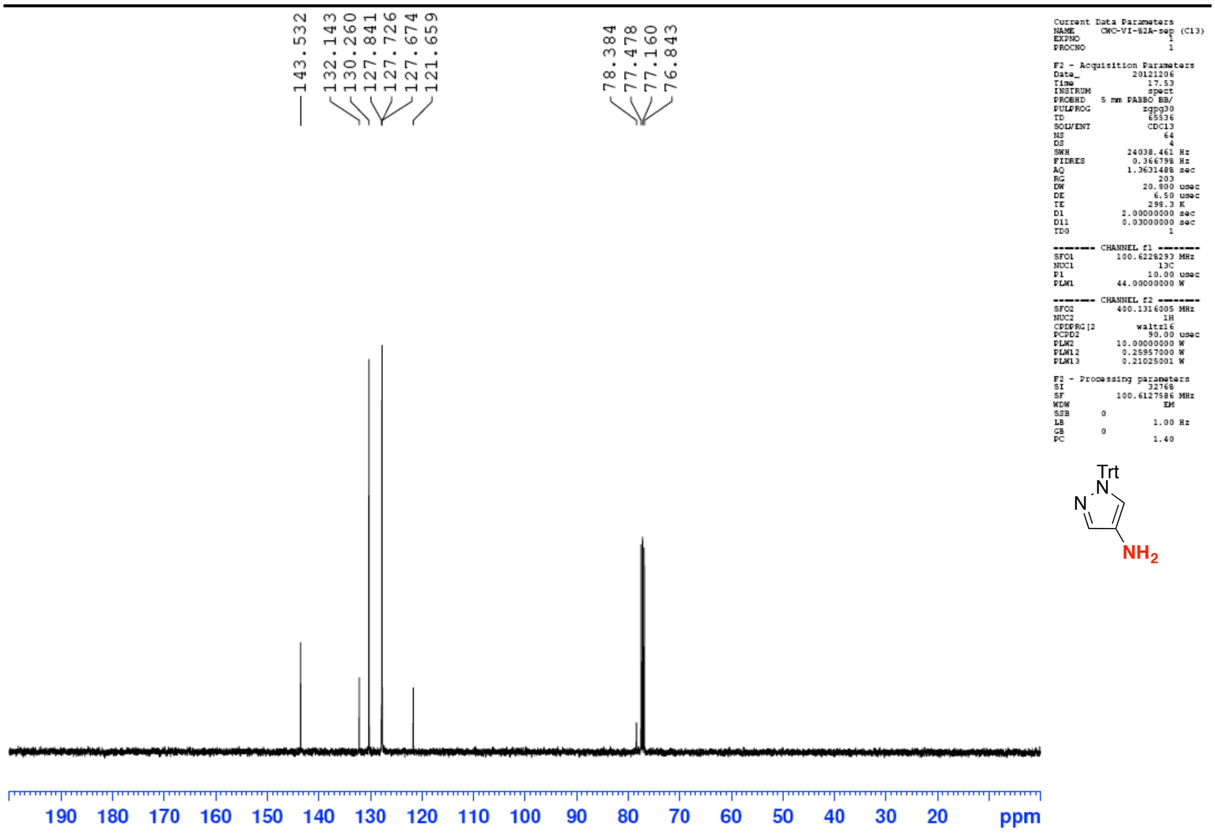




^{1}H and ^{13}C NMR of 4-Amino-1-trityl-1*H*-pyrazole (**7e**)

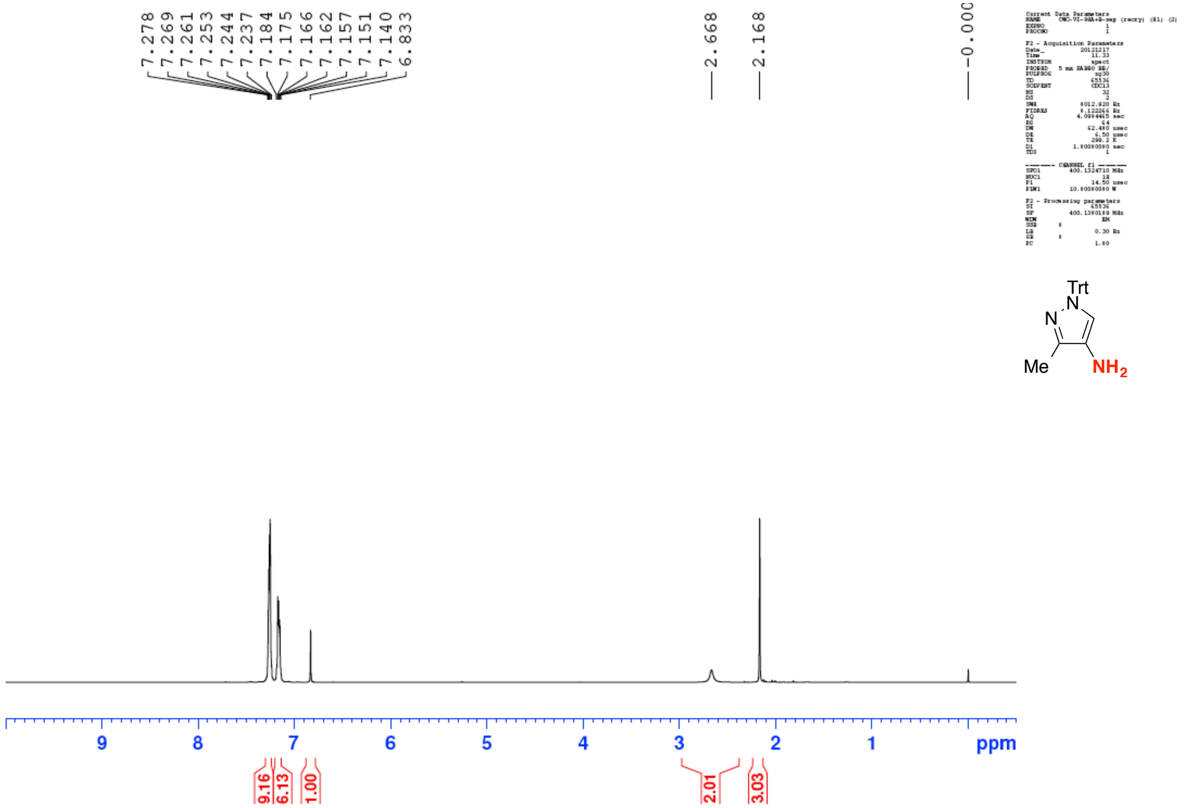


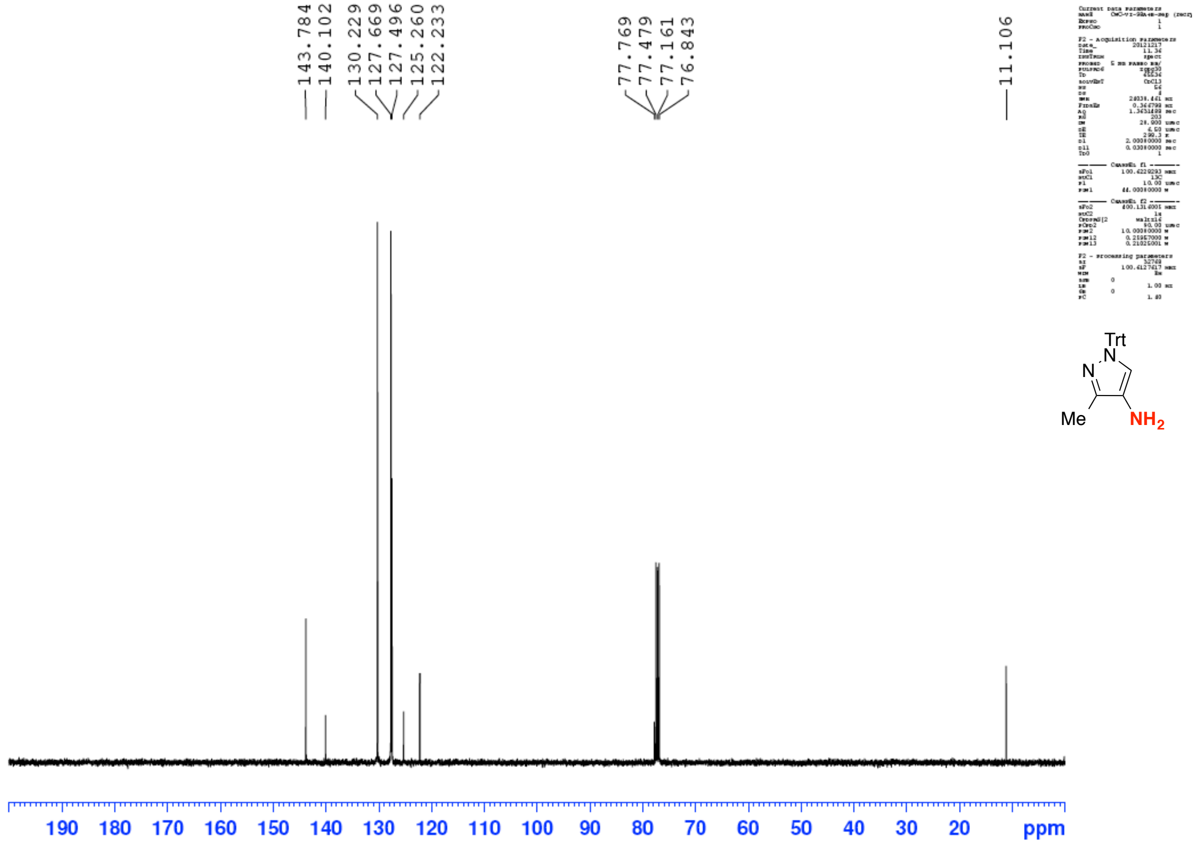
```
Current Data Parameters
NAME      CWC-VI-82A-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121206
Time                17.49
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     27
DS                      2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                     64
DW                 62.400 usec
DE                   6.50 usec
TE                  298.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  14.50 usec
PLW1         10.00000000 W

F2 - Processing parameters
SI                  65536
SF           400.1300145 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



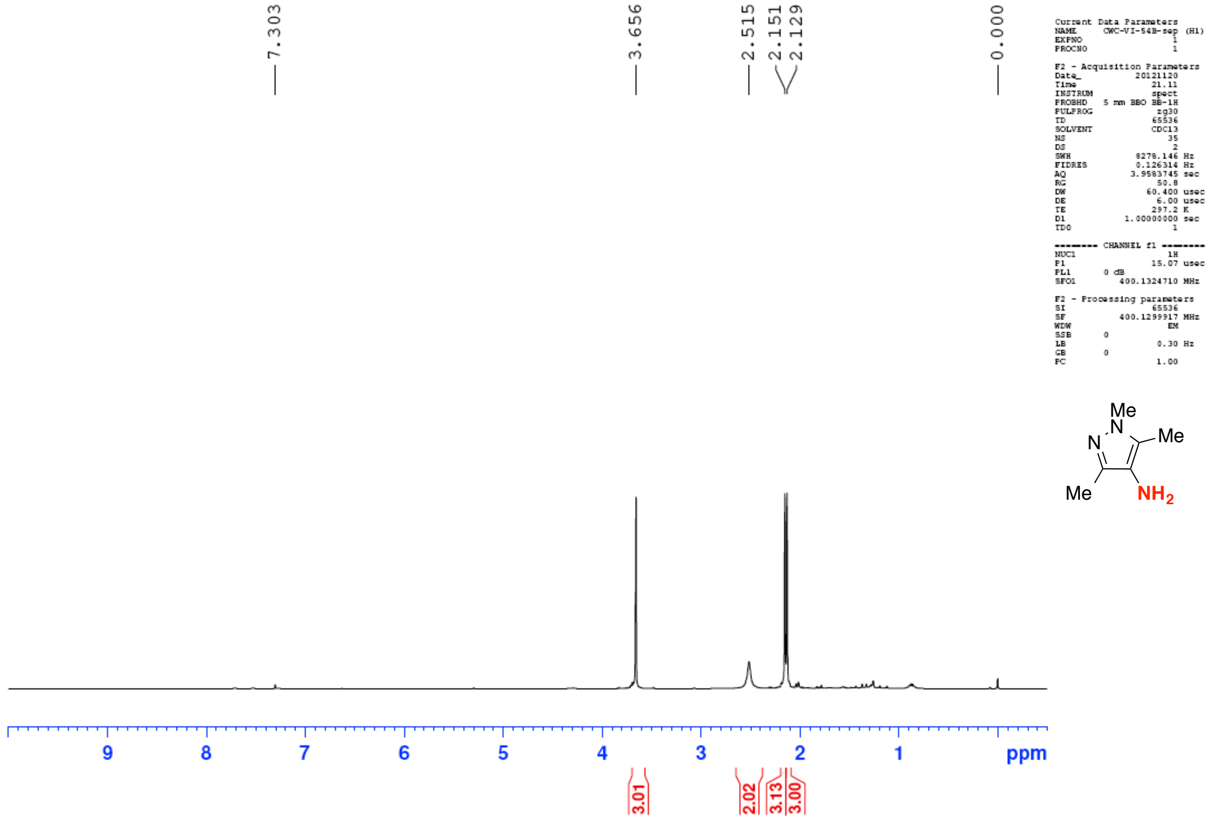
```
Current Data Parameters
NAME      CWC-VI-82A-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121206
Time                17.53
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                    203
DW                 20.800 usec
DE                   6.50 usec
TE                  298.3 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                  13C
P1                  10.00 usec
PLW1         44.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                   1H
CPDPRG[2         waltz16
PCPD2               90.00 usec
PLW2         10.00000000 W
PLW12         0.25957000 W
PLW13         0.21025001 W

F2 - Processing parameters
SI                  32768
SF           100.6127586 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

^{1}H and ^{13}C NMR of 3-methyl-4-amino-1-trityl-1*H*-pyrazole (**7f**)

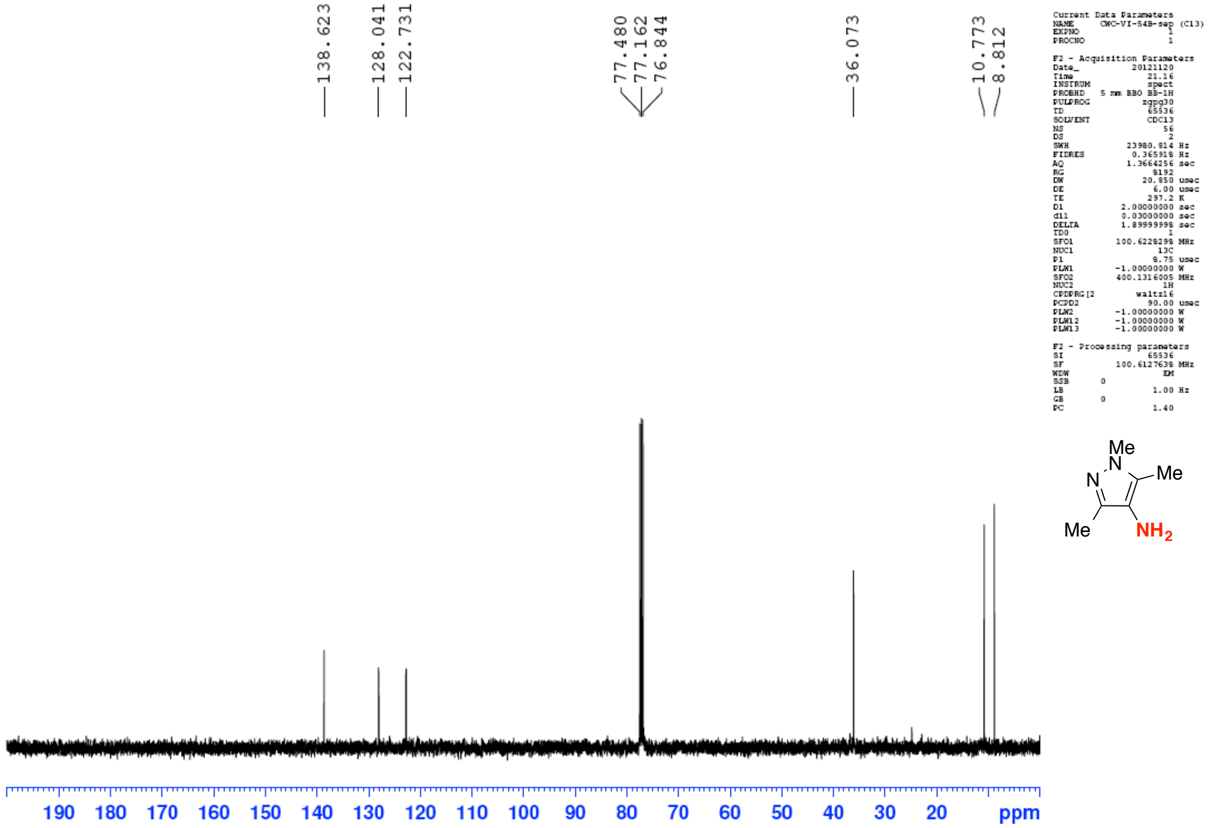




^{1}H and ^{13}C NMR of 4-Amino-1,3,5-trimethyl-1*H*-pyrazole (**7g**)

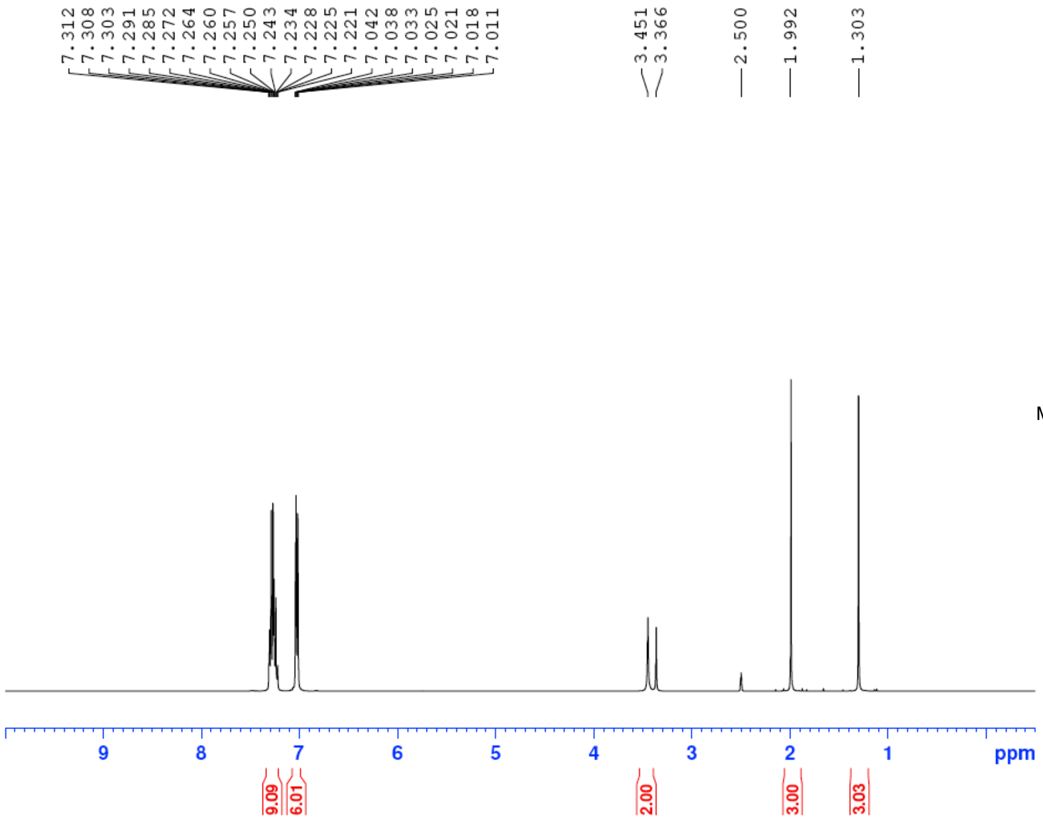


```
Current Data Parameters
NAME      CWC-VI-54B-sep (H1)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121120
Time                21.11
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     35
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                   50.8
DW                 60.400 usec
DE                   6.00 usec
TE                  297.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.07 usec
PL1      0 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  65536
SF            400.1299917 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

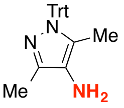


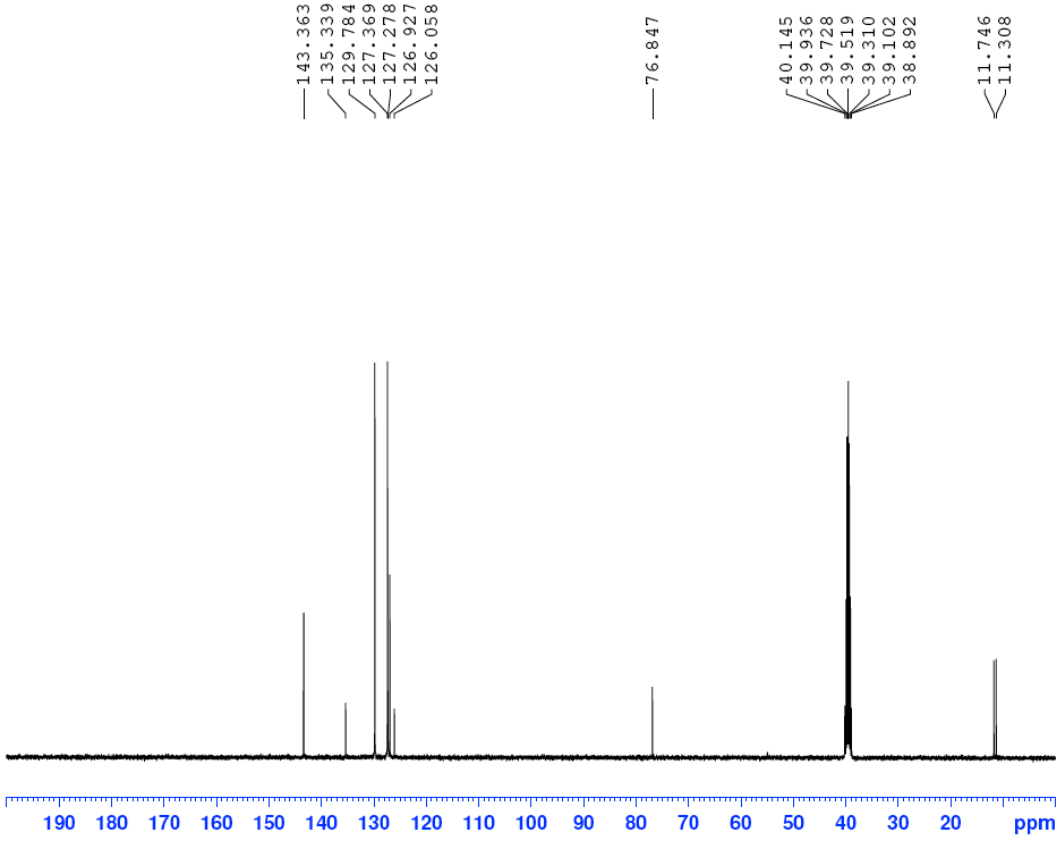
```
Current Data Parameters
NAME      CWC-VI-54B-sep (C13)
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20121120
Time                21.16
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     56
DS                      2
SWH             23980.814 Hz
FIDRES           0.365918 Hz
AQ              1.3664256 sec
RG                   8192
DW                 20.850 usec
DE                   6.00 usec
TE                  297.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
SFO1          100.6228298 MHz
NUC1                  13C
P1                   8.75 usec
PLW1          -1.00000000 W
SFO2          400.1316005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                  65536
SF            100.6127638 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

^{1}H and ^{13}C NMR of 4-Amino-3,5-dimethyl-1-trityl-1*H*-pyrazole (**7h**)



```
Current Data Parameters
NAME      CWC-VI-74A (sep) (3) (H1)
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20121205
Time              22.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   23
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894465 sec
RG                   57
DW               62.400 usec
DE                 6.50 usec
TE                295.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        400.1324710 MHz
NUC1                 1H
P1                14.50 usec
PLW1        10.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1319037 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```





```
Current Data Parameters
NAME      CWC-VI-74A (sep) (C1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20121205
Time              16.16
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                  125
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                294.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                10.00 usec
PLW1        44.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        10.00000000 W
PLW12        0.25957000 W
PLW13        0.21025001 W

F2 - Processing parameters
SI                32768
SF          100.6128148 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```