

Supporting Information for

Copper-Catalyzed, Ceric Ammonium Nitrate Mediated *N*-Arylation of Amines

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Contents

1. General Procedures	S2
2. ¹ H and ¹³ C NMR Data	S3
3. References	S11
4. ¹ H and ¹³ C NMR spectra	S13

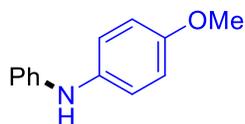
General method: Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in an oven or flame-dried glassware. All anhydrous solvents were distilled prior to use: THF, benzene, toluene, diethyl ether from Na and benzophenone; CH₂Cl₂, DMSO, DMF, hexane from CaH₂; MeOH, EtOH from Mg cake. Commercial reagents were used without purification. Column chromatography was carried out by using silica gel (100–200 mesh). ¹H and ¹³C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

Experimental Section

General Procedure: To a 5 mL scintillation vial equipped with a Teflon-coated magnetic stir bar were loaded with aryl/alkyl amine (1 equiv, 1 mmol), aryl boronic acid (1.2 equiv, 1.2 mmol), CAN (1.5 equiv, 1.5 mmol) and Cu(OAc)₂ (0.1 equiv, 0.1 mmol) in toluene at room temperature and stirred for 12-24 h. Monitored by TLC until the starting materials were consumed. The solvent was removed by rotavapor to give a residue, from which the product was isolated by column chromatography on silica gel with MeOH/CH₂Cl₂ or EtOAc/petroleum ether (1% Et₃N as modifier) as eluents. Appropriate fractions were evaporated to afford the desired product.

Table 1:**3a: 4-Methoxy-*N*-phenylaniline**

The compound data were in accordance with the literature.¹

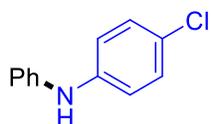


¹H NMR (300 MHz, CDCl₃) δ 7.25 (dd, *J* = 10.2, 5.3 Hz, 2H), 7.10 (s, 2H), 7.01 – 6.72 (m, 5H), 5.30 (s, 1H), 3.84 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 155.3, 145.1, 135.7, 129.2, 122.1, 119.6, 115.6, 114.6, 55.5.

4a: 4-Chloro-*N*-phenylaniline

The compound data were in accordance with the literature.¹

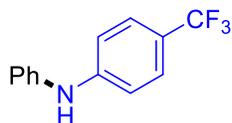


¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.16 (m, 4H), 7.12 – 6.92 (m, 5H), 5.68 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 142.6, 141.8, 129.4, 129.4, 129.3, 125.5, 121.5, 118.8, 118.1.

4b: *N*-phenyl-4-(trifluoromethyl)aniline

The compound data were in accordance with the literature.²

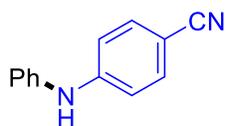


¹H NMR (300 MHz, CDCl₃) δ 7.49 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.31 (m, 2H), 7.17 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.12 – 6.99 (m, 3H), 5.92 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 146.8, 141.2, 129.6, 126.7 (q, *J* = 3.8 Hz), 124.6, 122.9, 121.7 (q, *J* = 32.4), 120.0, 115.3.

4c: 4-(phenylamino)benzotrile

The compound data were in accordance with the literature.²

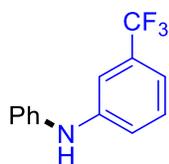


¹H NMR (300 MHz, CDCl₃) δ 7.53 – 7.43 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 1.3 Hz, 2H), 7.14 (ddd, *J* = 14.7, 8.5, 1.0 Hz, 1H), 7.03 – 6.92 (m, 2H), 6.05 (s, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 148.0, 140.0, 133.8, 129.6, 124.0, 121.3, 119.7, 114.9, 101.7.

4d: *N*-phenyl-3-(trifluoromethyl)aniline

The compound data were in accordance with the literature.³

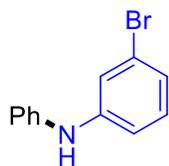


¹H NMR (300 MHz, CDCl₃) δ 7.38 – 7.30 (m, 3H), 7.28 (dd, *J* = 4.9, 4.3 Hz, 1H), 7.23 – 7.17 (m, 1H), 7.17 – 7.08 (m, 3H), 7.08 – 6.96 (m, 1H), 5.65 (s, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 144.0, 141.8, 131.6 (q, *J* = 33 Hz), 129.8, 129.5, 124.1 (q, *j* = 180 Hz), 122.3, 119.7, 119.1, 116.9 (q, *j* = 4 Hz), 113.2.

4e: 3-bromo-*N*-phenylaniline

The compound data were in accordance with the literature.⁴

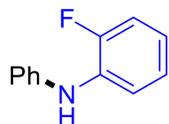


¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.28 (m, 2H), 7.23 (dt, *J* = 4.1, 2.3 Hz, 1H), 7.18 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 7.00 – 6.91 (m, 1H), 5.71 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 144.9, 141.9, 130.7, 129.5, 123.4, 123.2, 122.2, 119.6, 119.0, 115.6.

4f: 2-fluoro-*N*-phenylaniline

The compound data were in accordance with the literature.⁵

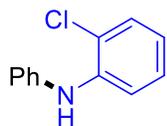


^1H NMR (300 MHz, CDCl_3) δ 7.51 – 7.19 (m, 2H), 7.17 – 6.86 (m, 6H), 6.88 – 6.69 (m, 1H), 5.76 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 152.9 (d, $J = 241.0$ Hz), 141.9, 129.3, 124.2, 124.2, 121.7, 120.4 (d, $J = 7.3$ Hz), 118.6, 117.1, 115.4 (d, $J = 19.2$ Hz).

4g: 2-chloro-*N*-phenylaniline

The compound data were in accordance with the literature.⁶

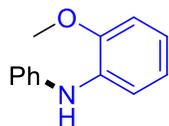


^1H NMR (300 MHz, CDCl_3) δ 7.51 – 7.25 (m, 4H), 7.25 – 6.96 (m, 4H), 6.85 (t, $J = 7.6$ Hz, 1H), 6.15 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 141.5, 140.3, 129.8, 129.5, 127.5, 122.7, 121.5, 120.4, 120.2, 115.6.

4h: 2-methoxy-*N*-phenylaniline

The compound data were in accordance with the literature.⁶

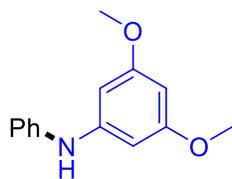


^1H NMR (600 MHz, CDCl_3) δ 7.45 – 7.28 (m, 3H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.08 – 6.93 (m, 4H), 6.26 (s, 1H), 3.98 – 3.94 (m, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 148.3, 142.8, 133.0, 129.3, 121.2, 120.9, 119.9, 118.6, 114.8, 110.6, 55.6.

4i: 3,5-dimethoxy-*N*-phenylaniline

The compound data were in accordance with the literature.¹

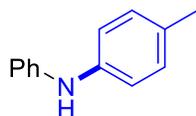


¹H NMR (300 MHz, CDCl₃) δ 7.44 – 7.21 (m, 2H), 7.18 – 7.05 (m, 2H), 7.04 – 6.83 (m, 1H), 6.32 – 6.17 (m, 2H), 6.13 – 5.97 (m, 1H), 5.72 (s, 1H), 3.82 – 3.69 (m, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 161.6, 145.2, 142.5, 129.3, 121.4, 118.8, 95.7, 92.9, 55.3.

4j: 4-methyl-N-phenylaniline

The compound data were in accordance with the literature.¹

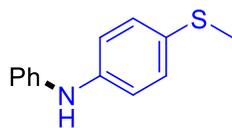


¹H NMR (300 MHz, CDCl₃) δ 7.32 – 7.19 (m, 2H), 7.16 – 6.96 (m, 6H), 6.90 (t, *J* = 7.1 Hz, 1H), 5.61 (s, 1H), 2.33 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.9, 140.3, 131.0, 129.9, 129.3, 129.1, 120.3, 118.9, 116.9, 20.7.

4k: 4-(methylthio)-N-phenylaniline

The compound data were in accordance with the literature.⁷



¹H NMR (300 MHz, CDCl₃) δ 7.30 – 7.22 (m, 4H), 7.11 – 6.98 (m, 4H), 6.93 (dt, *J* = 18.7, 6.1 Hz, 1H), 5.68 (s, 1H), 2.46 (d, *J* = 4.3 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.0, 141.3, 129.9, 129.4, 129.0, 121.1, 118.5, 117.7, 17.9.

4l: N-phenylpyridin-2-amine

The compound data were in accordance with the literature.⁵



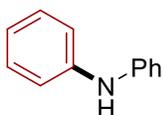
^1H NMR (300 MHz, CDCl_3) δ 8.20 (s, 1H), 7.50 (t, $J = 7.8$ Hz, 1H), 7.40 – 7.15 (m, 4H), 7.13 – 6.97 (m, 1H), 6.96 – 6.79 (m, 2H), 6.77 – 6.61 (m, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 155.9, 147.7, 140.1, 138.0, 129.3, 123.1, 120.6, 114.9, 108.3.

Table 2:

6a: Diphenylamine

The compound data were in accordance with the literature.¹

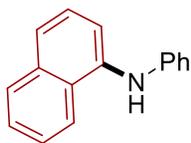


^1H NMR (300 MHz, CDCl_3) δ 7.49 – 7.24 (m, 4H), 7.17 (d, $J = 8.1$ Hz, 4H), 7.04 (t, $J = 7.3$ Hz, 2H), 5.65 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 143.0, 129.3, 120.9, 117.7.

6b: N-Phenylnaphthalen-1-amine

The compound data were in accordance with the literature.¹

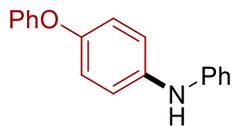


^1H NMR (300 MHz, CDCl_3) δ 8.19 – 8.02 (m, 1H), 7.99 – 7.87 (m, 1H), 7.64 (dd, $J = 5.7, 2.8$ Hz, 1H), 7.60 – 7.49 (m, 2H), 7.49 – 7.40 (m, 2H), 7.39 – 7.25 (m, 2H), 7.07 (dd, $J = 8.7, 2.3$ Hz, 2H), 7.04 – 6.93 (m, 1H), 6.05 (brs, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 144.5, 138.5, 134.7, 129.4, 128.6, 127.8, 126.2, 126.1, 125.8, 123.3, 121.9, 120.8, 117.6, 116.2.

6c: 4-Phenoxyphenylphenylamine

The compound data were in accordance with the literature.⁸

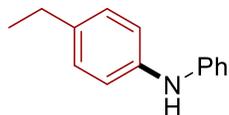


¹H NMR (300 MHz, CDCl₃) δ 7.30 (dddd, *J* = 8.4, 7.4, 4.8, 2.1 Hz, 4H), 7.15 – 6.87 (m, 10H), 5.62 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 158.5, 151.6, 144.2, 130.0, 129.9, 129.7, 123.0, 120.9, 120.9, 120.7, 118.3, 118.2, 117.2.

6d: 4-Ethyl-N-phenylaniline

The compound data were in accordance with the literature.¹

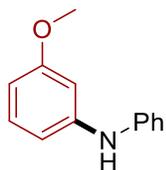


¹H NMR (300 MHz, CDCl₃) δ 7.36 – 7.19 (m, 2H), 7.42 – 6.83 (m, 2H), 7.07 (dd, *J* = 5.2, 3.2 Hz, 4H), 6.95 (dd, *J* = 10.5, 4.2 Hz, 1H), 5.65 (s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.9, 140.6, 137.4, 129.4, 128.7, 120.4, 118.9, 118.8, 117.0, 28.2, 15.8.

6e: 3-Methoxy-N-phenylaniline

The compound data were in accordance with the literature.¹

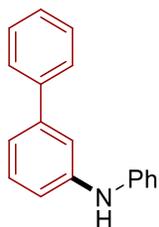


^1H NMR (600 MHz, CDCl_3) δ 7.24 (t, $J = 7.7$ Hz, 2H), 7.13 (t, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 7.9$ Hz, 2H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 8.5$ Hz, 2H), 6.46 (d, $J = 8.2$ Hz, 1H), 5.68 (s, 1H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 160.8, 144.7, 142.9, 130.2, 129.4, 121.3, 118.4, 110.3, 106.3, 103.4, 55.3.

6f: *N*-(3-Biphenyl)aniline

The compound data were in accordance with the literature.⁹



^1H NMR (300 MHz, CDCl_3) δ 7.65 (ddd, $J = 4.3, 3.5, 1.9$ Hz, 2H), 7.50 (ddd, $J = 7.6, 4.5, 1.3$ Hz, 2H), 7.46 – 7.33 (m, 5H), 7.30 – 7.16 (m, 3H), 7.16 – 7.09 (m, 1H), 7.03 (ddd, $J = 8.4, 2.2, 1.1$ Hz, 1H), 5.82 (s, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 143.5, 142.9, 142.4, 141.1, 129.6, 129.3, 128.7, 127.3, 127.1, 121.1, 119.8, 117.9, 116.5, 116.4.

6g: *N*-(3-Fluorophenyl)-*N*-phenylamine

The compound data were in accordance with the literature.¹⁰

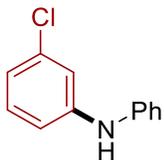


^1H NMR (300 MHz, CDCl_3) δ 7.46 – 7.28 (m, 2H), 7.27 – 7.10 (m, 3H), 7.04 (dt, $J = 14.6, 4.1$ Hz, 1H), 6.88 – 6.73 (m, 2H), 6.72 – 6.65 (m, 1H), 5.78 (s, 1H).

^{13}C NMR (151 MHz, CDCl_3) δ 163.8 (d, $J = 243.9$ Hz), 145.4 (d, $J = 10.5$ Hz), 141.9, 130.4 (d, $J = 10.0$ Hz), 129.4, 122.0, 119.0, 112.4, 106.9 (d, $J = 21.5$ Hz), 103.5 (d, $J = 25.1$ Hz).

6h: 3-Chloro-*N*-phenylaniline

The compound data were in accordance with the literature.¹¹



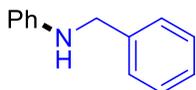
¹H NMR (300 MHz, CDCl₃) δ 7.42 – 7.23 (m, 2H), 7.3-6.9 (m, *J* = 15.9, 7.7 Hz, 5H), 6.91 (dd, *J* = 9.2, 4.0 Hz, 2H), 5.70 (s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 144.8, 141.9, 135.0, 130.3, 129.5, 122.1, 120.5, 119.0, 116.6, 115.1.

Table 3:

8a: *N*-benzylaniline

The compound data were in accordance with the literature.¹¹

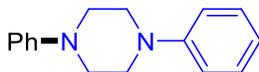


¹H NMR (300 MHz, CDCl₃) δ 7.41 – 7.26 (m, 5H), 7.24 – 7.15 (m, 2H), 6.79 – 6.69 (m, 1H), 6.69 – 6.60 (m, 2H), 4.34 (s, 2H), 4.08 (bs, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 148.1, 139.4, 129.3, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3.

8b: 1,4-Diphenylpiperazine

The compound data were in accordance with the literature.¹²

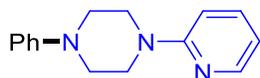


¹H NMR (300 MHz, CDCl₃) δ 7.32 – 7.25 (m, 4H), 6.99 (dd, *J* = 7.9, 0.7 Hz, 4H), 6.90 (td, *J* = 7.3, 0.7 Hz, 2H), 3.34 (d, *J* = 4.9 Hz, 8H).

¹³C NMR (151 MHz, CDCl₃) δ 151.3, 129.3, 129.2, 120.1, 116.4, 49.5.

8c: 1-Phenyl-4-(pyridin-2-yl)piperazine

The compound data were in accordance with the literature.¹²

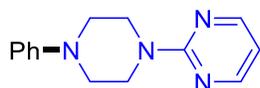


^1H NMR (300 MHz, CDCl_3) δ 8.22 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.52 (ddd, $J = 8.9, 7.2, 2.0$ Hz, 1H), 7.34 – 7.26 (m, 2H), 6.98 (dd, $J = 13.0, 5.1$ Hz, 2H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.75 – 6.62 (m, 2H), 3.71 (dd, $J = 6.1, 4.3$ Hz, 4H), 3.31 (dd, $J = 6.1, 4.3$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 159.2, 151.2, 147.6, 137.9, 129.2, 120.1, 116.4, 113.6, 107.5, 49.2, 45.4.

8d: 2-(4-Phenylpiperazin-1-yl)pyrimidine

The compound data were in accordance with the literature.¹³



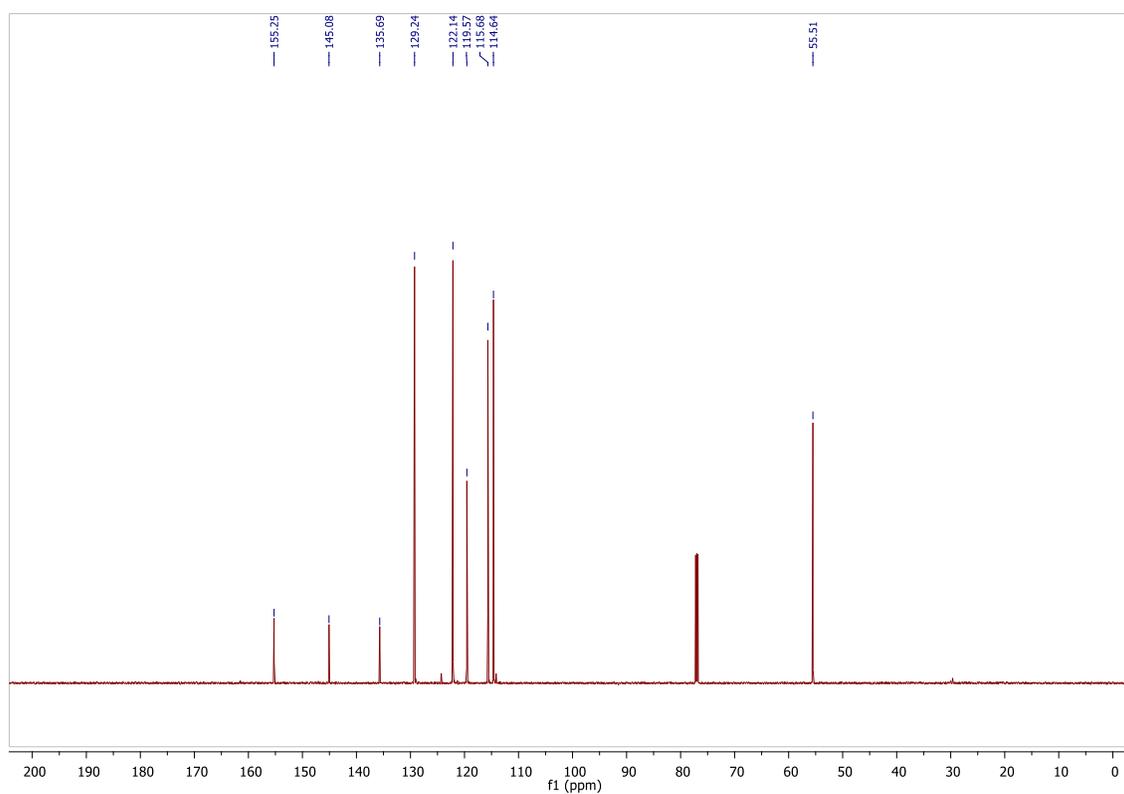
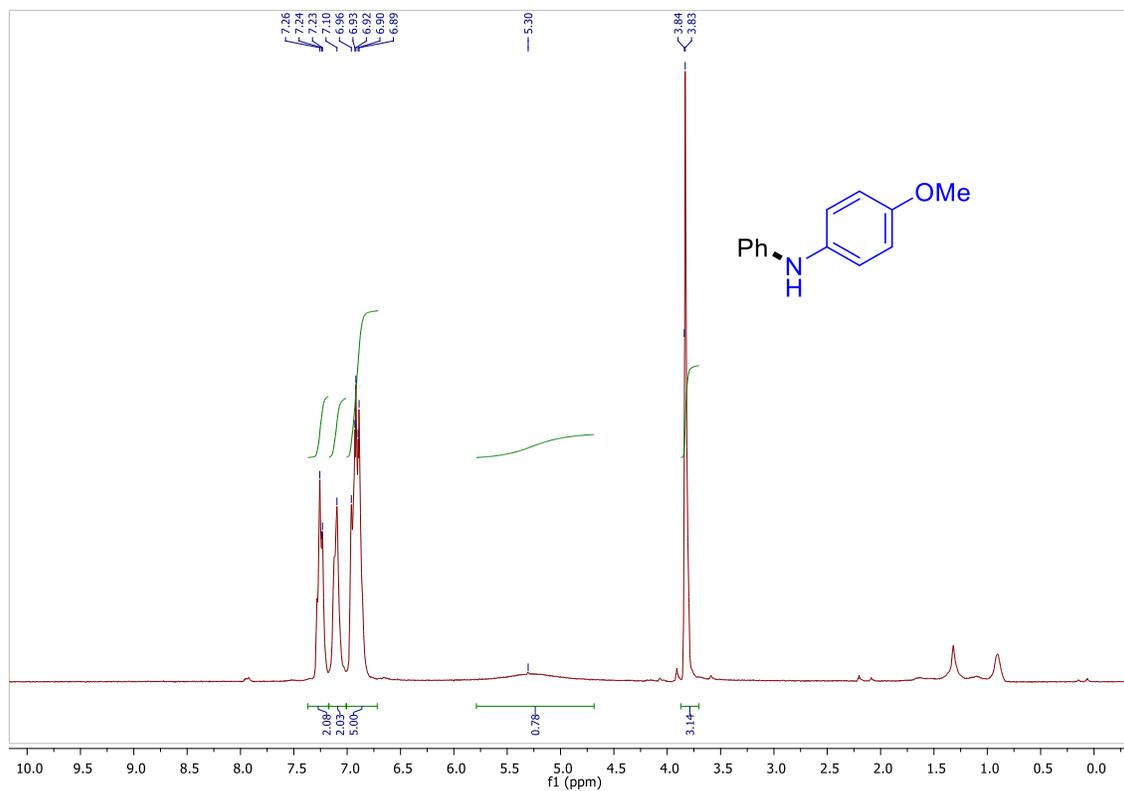
^1H NMR (300 MHz, CDCl_3) δ 8.55 – 8.18 (m, 2H), 7.44 – 7.17 (m, 3H), 7.03 – 6.94 (m, 1H), 6.94 – 6.84 (m, 1H), 6.52 (dd, $J = 6.2, 3.2$ Hz, 1H), 4.10 – 3.88 (m, 4H), 3.23 (dd, $J = 23.1, 18.0$ Hz, 4H).

^{13}C NMR (151 MHz, CDCl_3) δ 161.7, 157.8, 151.3, 129.2, 120.2, 116.5, 110.1, 49.4, 43.7.

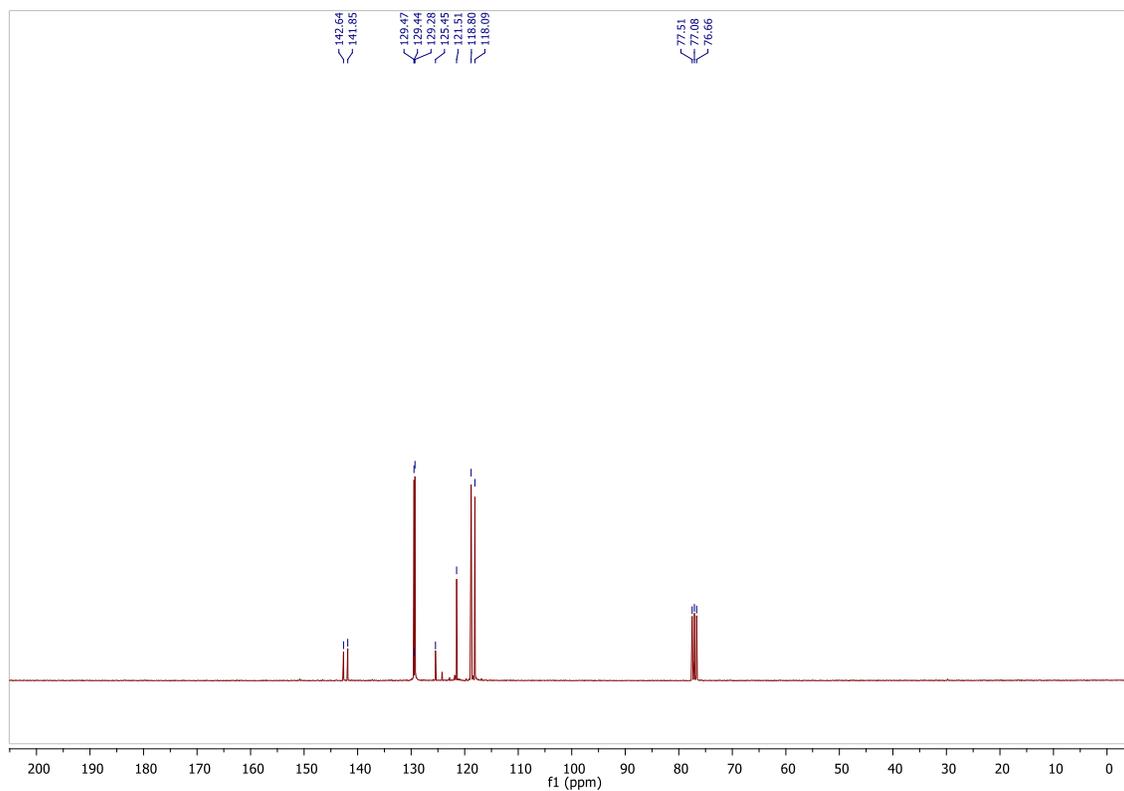
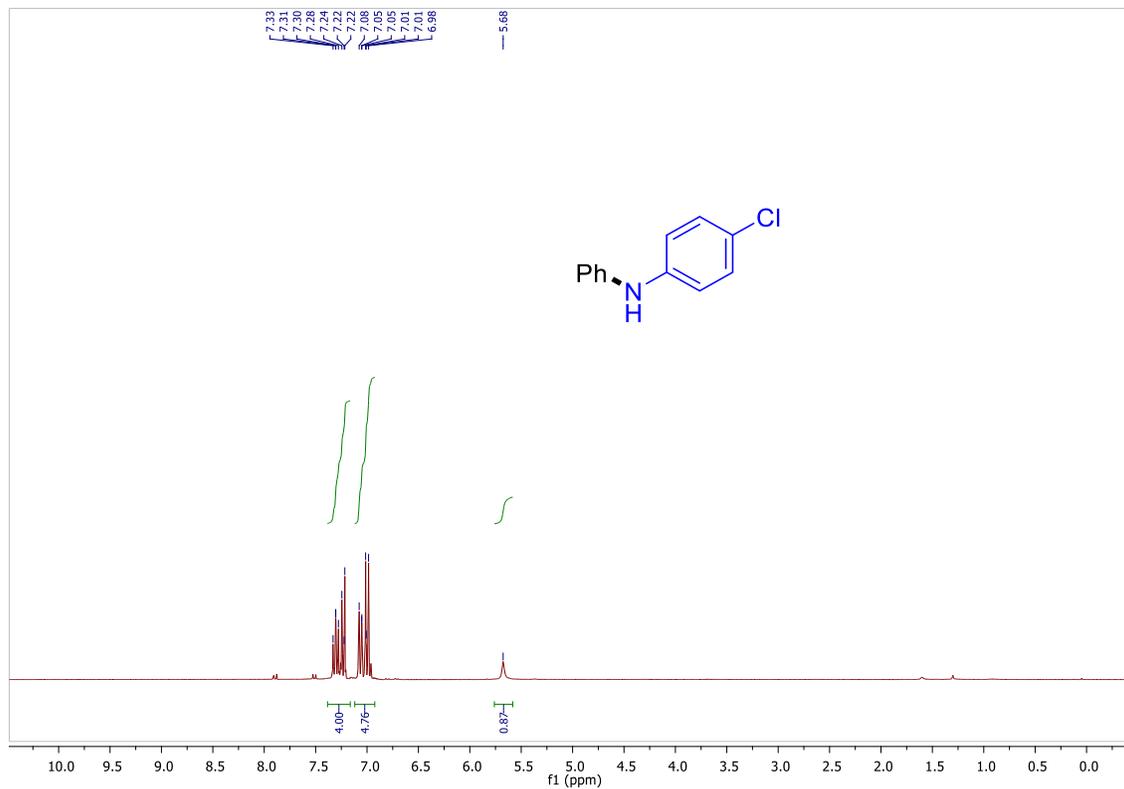
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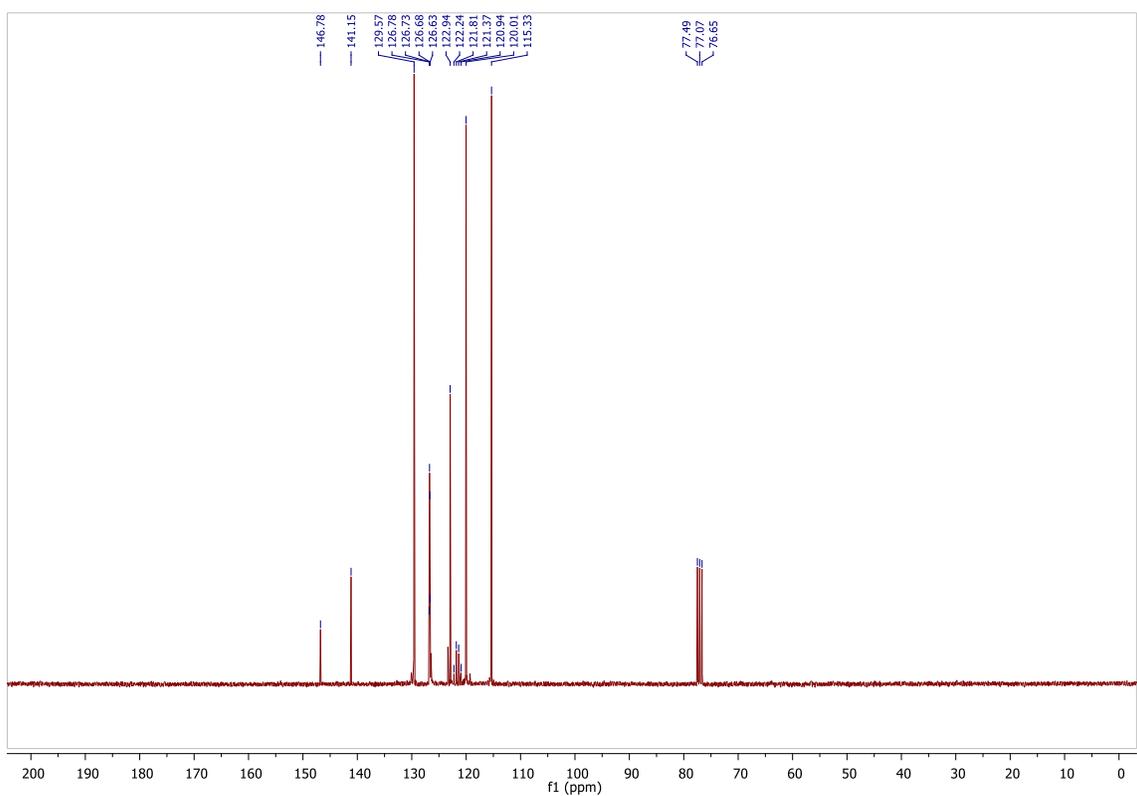
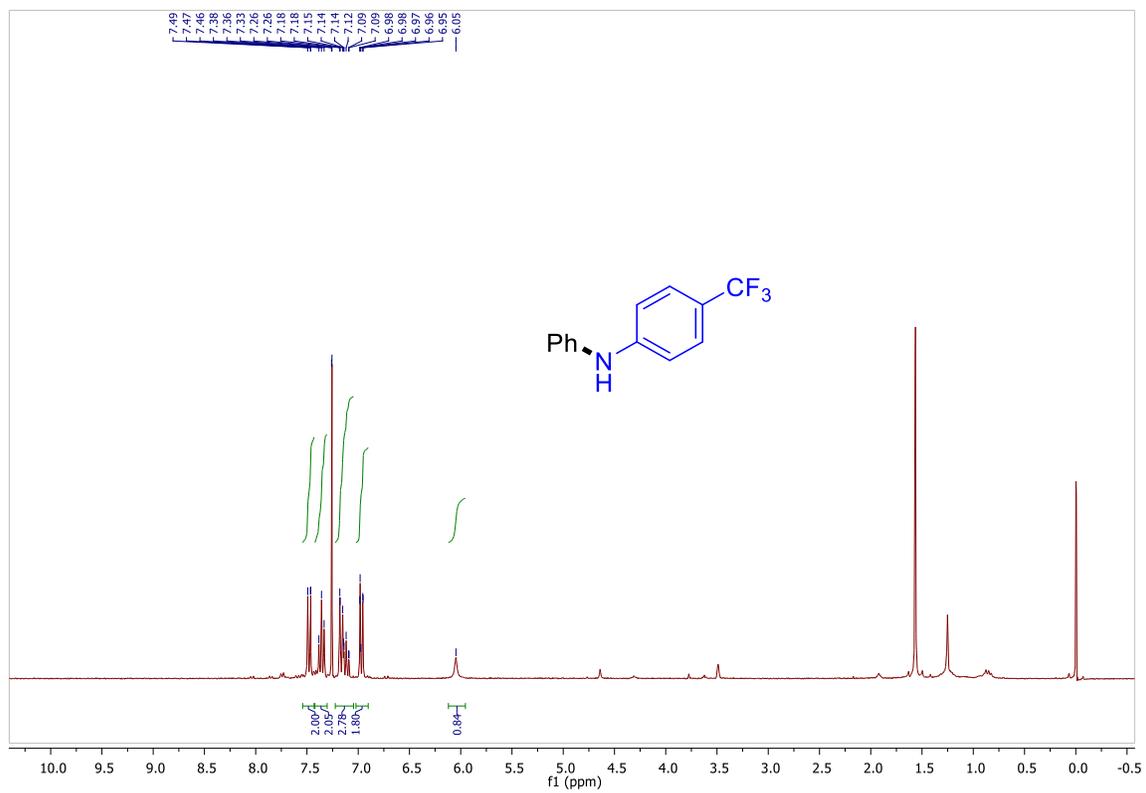
- ⁹ L. Ilies, T. Matsubara, E. Nakamura, *Org. Lett.*, 2012, **14**, 5570-5573.
- ¹⁰ C. Desmarets, R. Schneider, Y. Fort, *J. Org. Chem.* 2002, **67**, 3029-3036.
- ¹¹ W-B. Sun, P-Z. Zhang, T. Jiang, C.-K. Li, L-T. An, A. Shoberu, J.-P. Zou, *Tetrahedron* 2016, **72**, 6477-6483.
- ¹² Lin, Y.; Li, M.; Ji, X.; Wu, J.; Cao, S. *Tetrahedron* 2017, **73**, 1466-1472.
- ¹³ L. A. Ho, C. L. Raston, K. A. Stubbs, *Eur. J. Org. Chem.* 2016, 5957–5963.



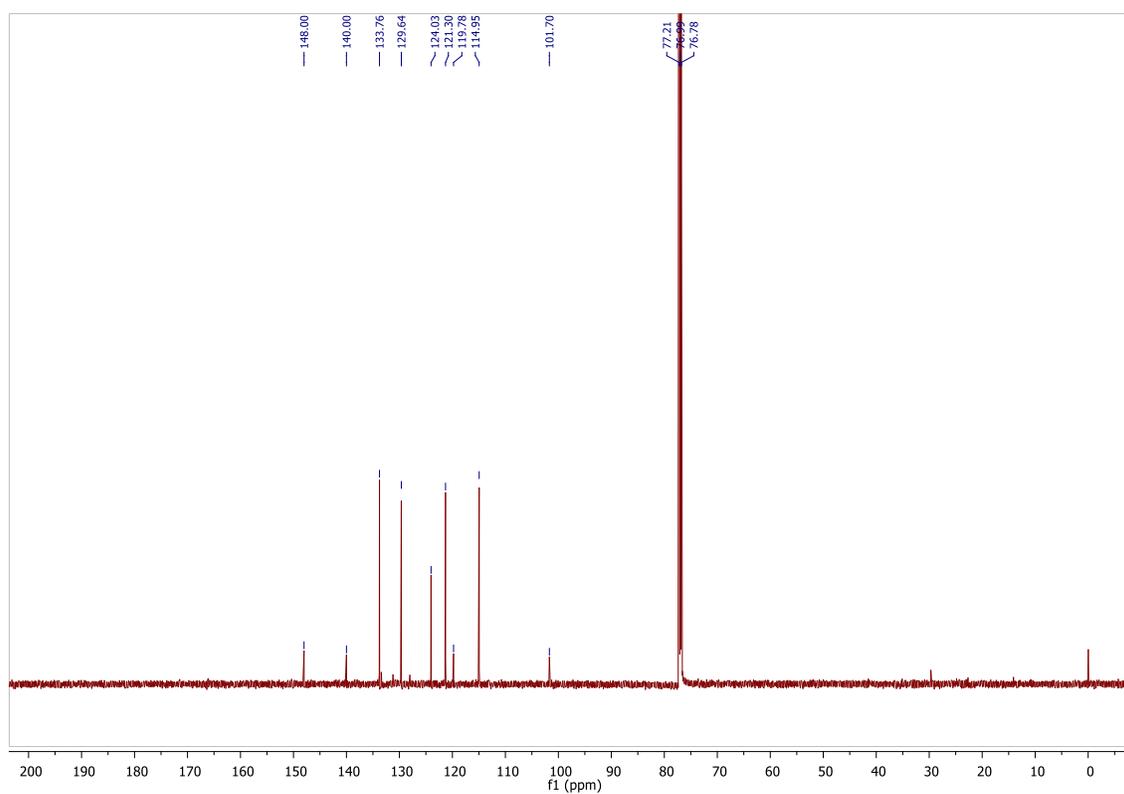
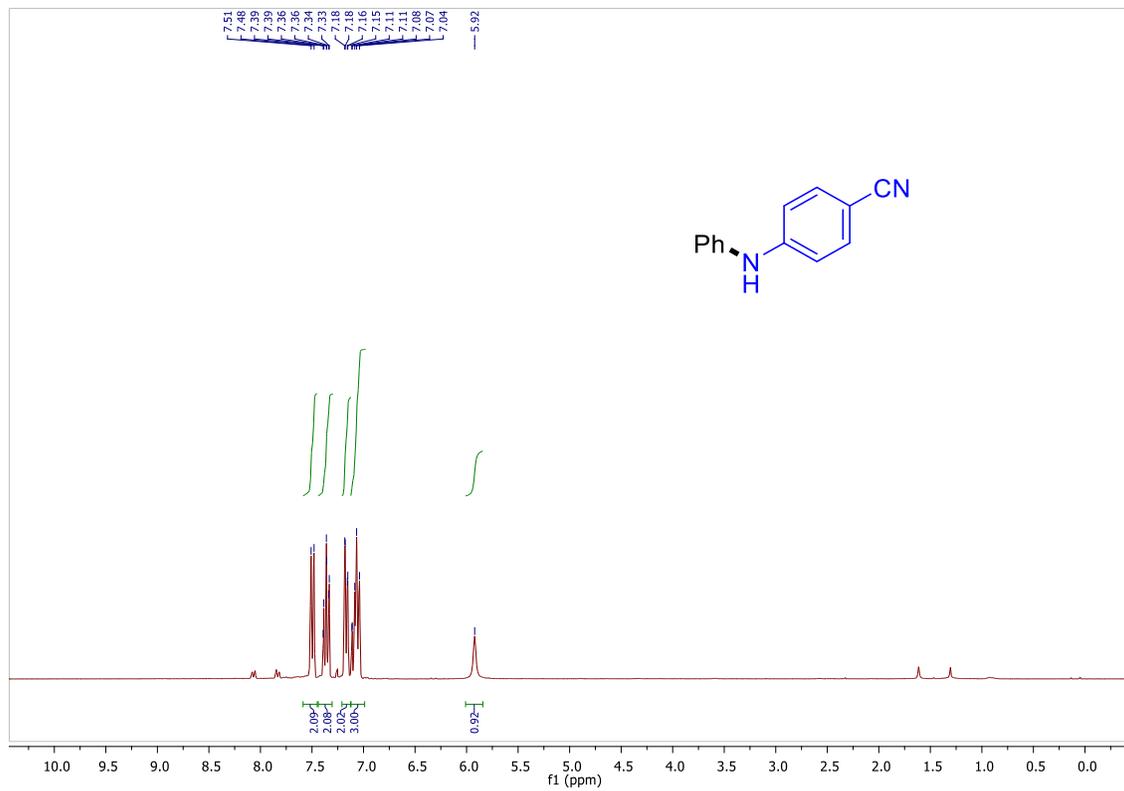
¹H and ¹³C NMR of 4-Methoxy-N-phenylaniline (3a)



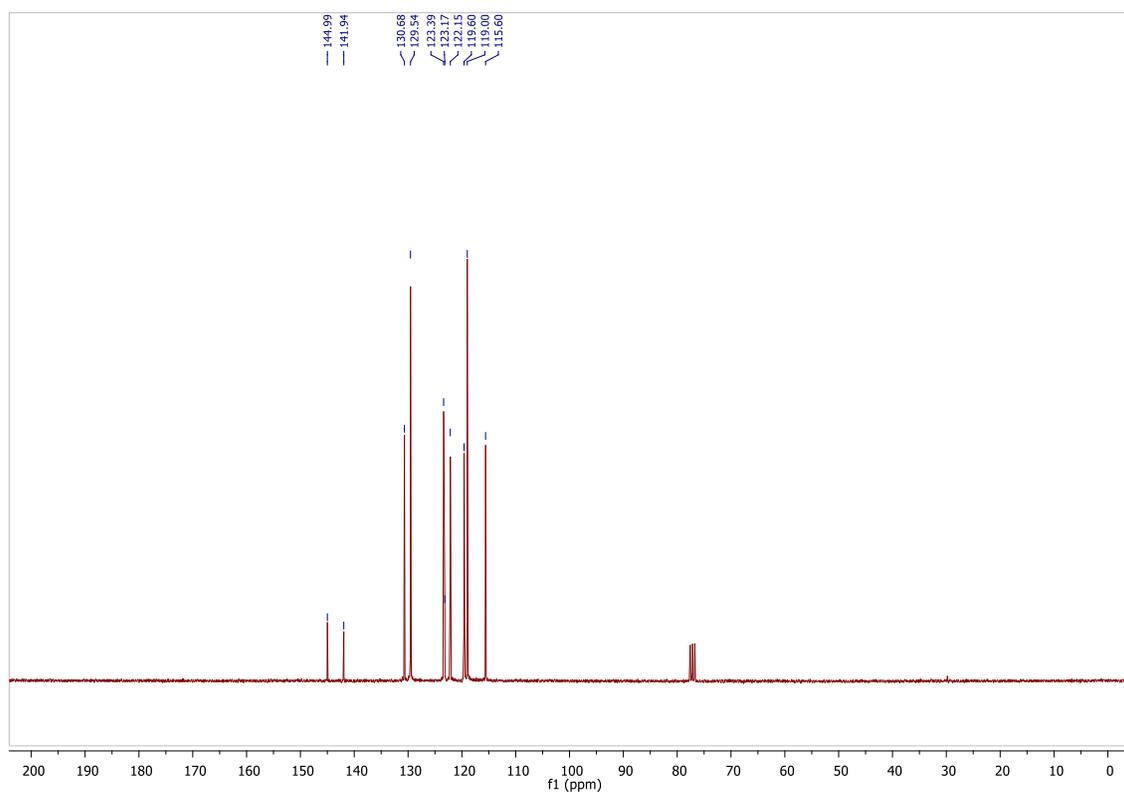
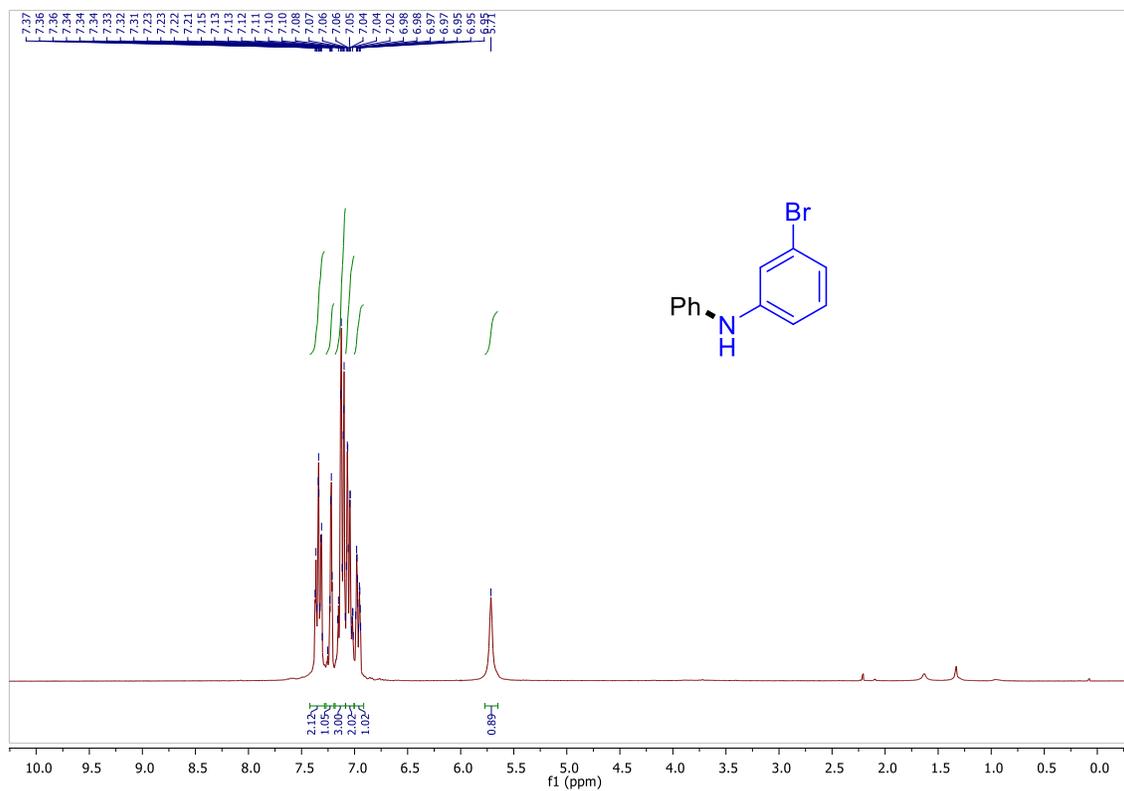
¹H and ¹³C NMR of **4-Chloro-N-phenylaniline (4a)**



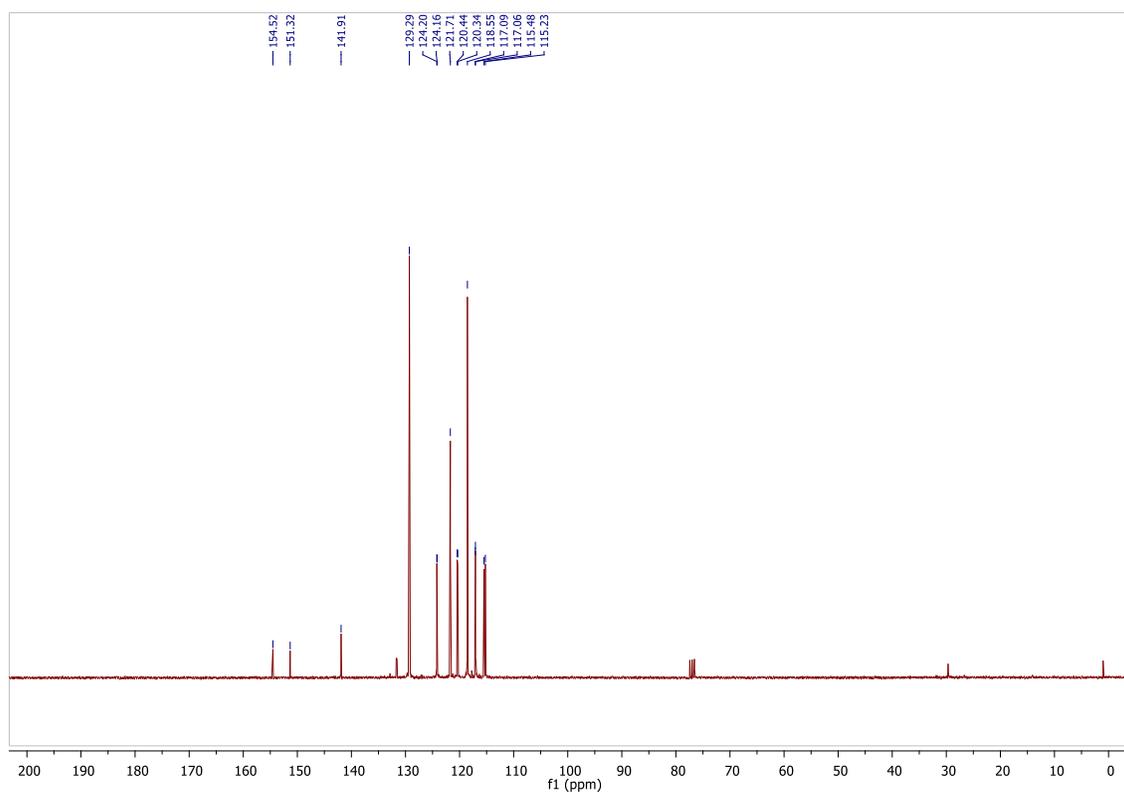
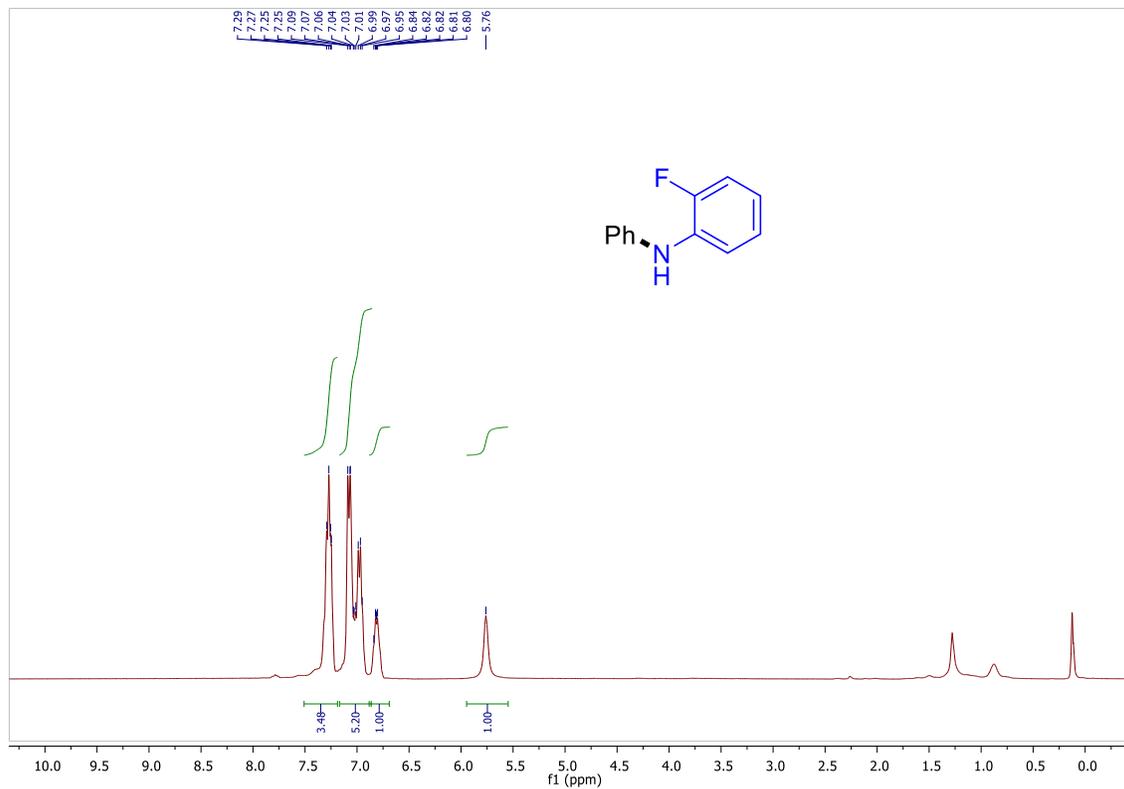
¹H and ¹³C NMR of N-phenyl-4-(trifluoromethyl)aniline (4b)



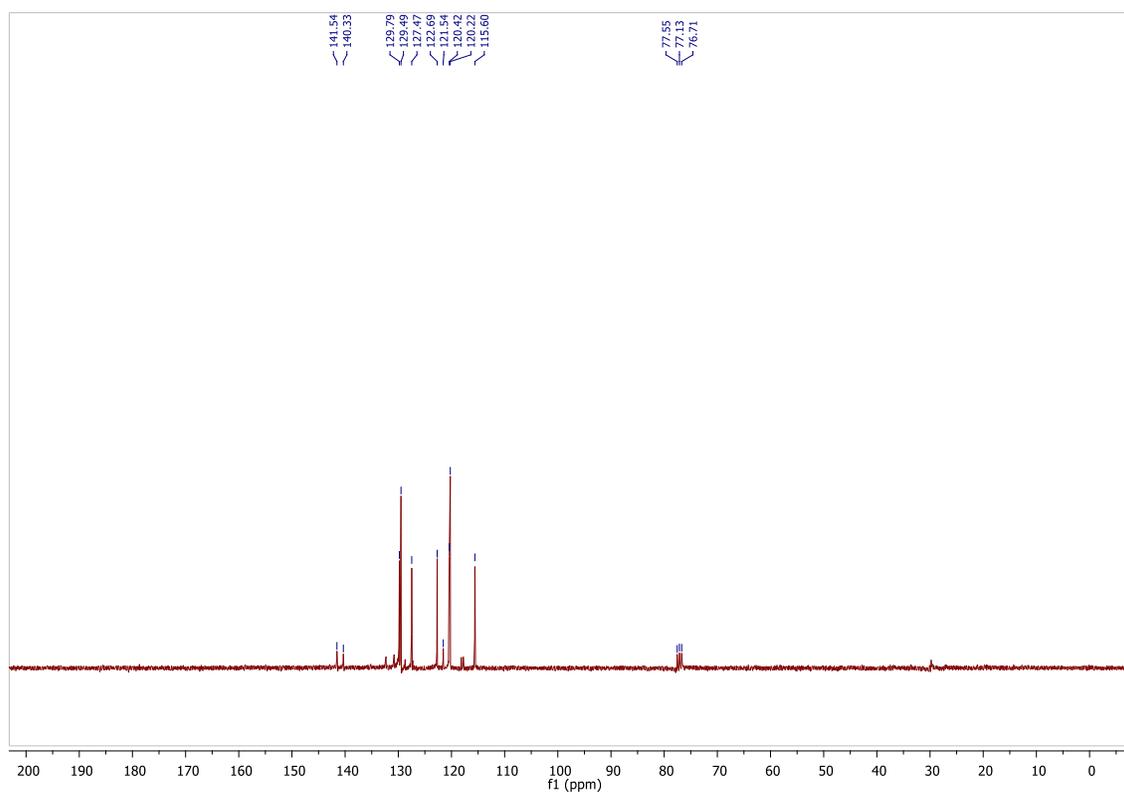
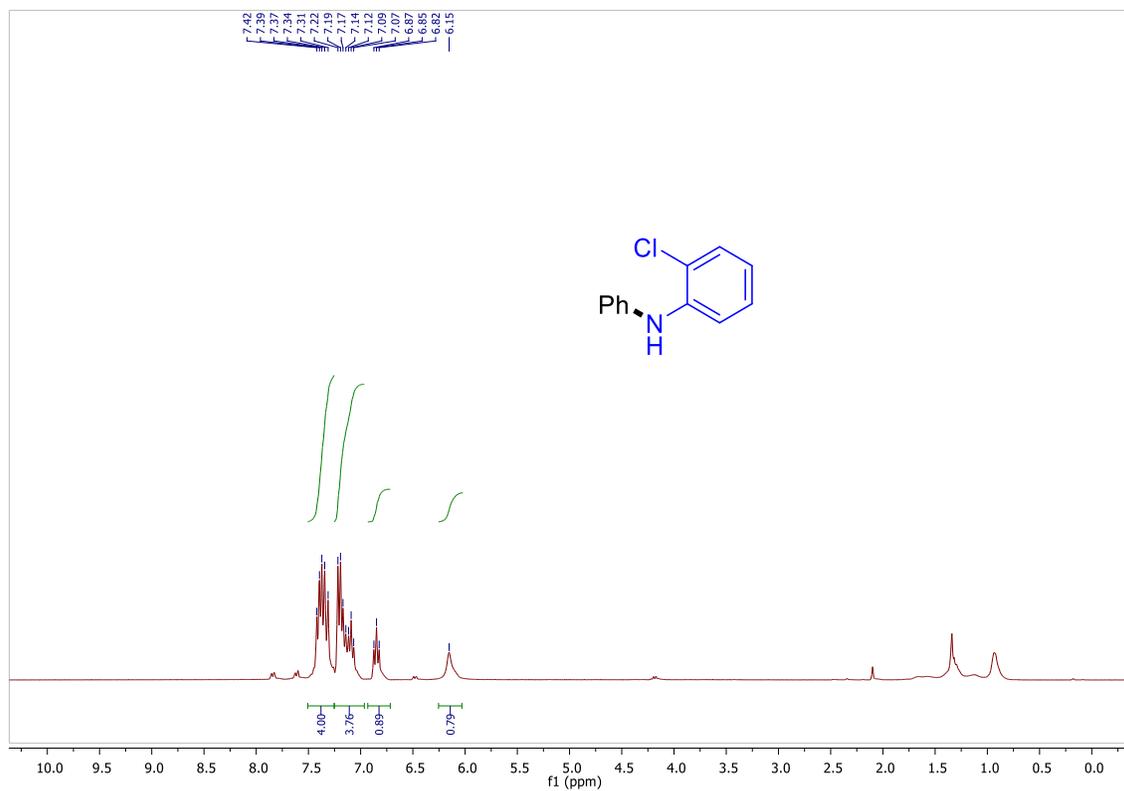
^1H and ^{13}C NMR of 4-(phenylamino)benzonitrile (4c)



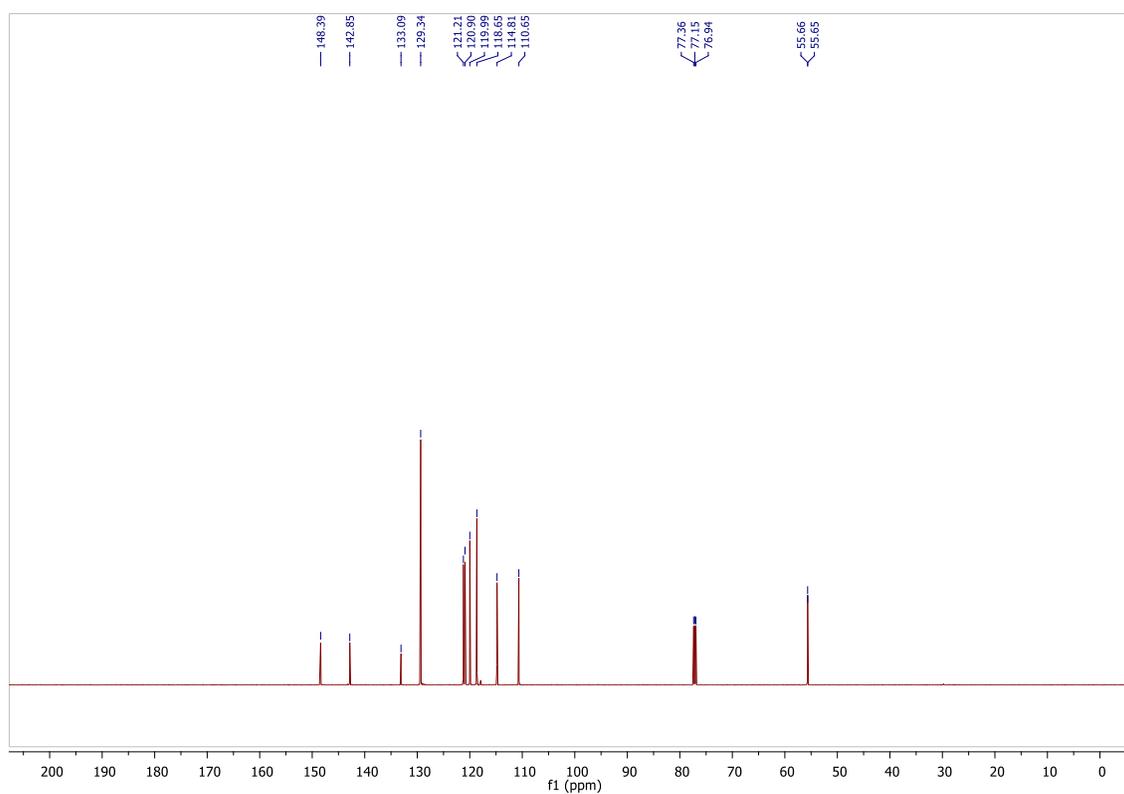
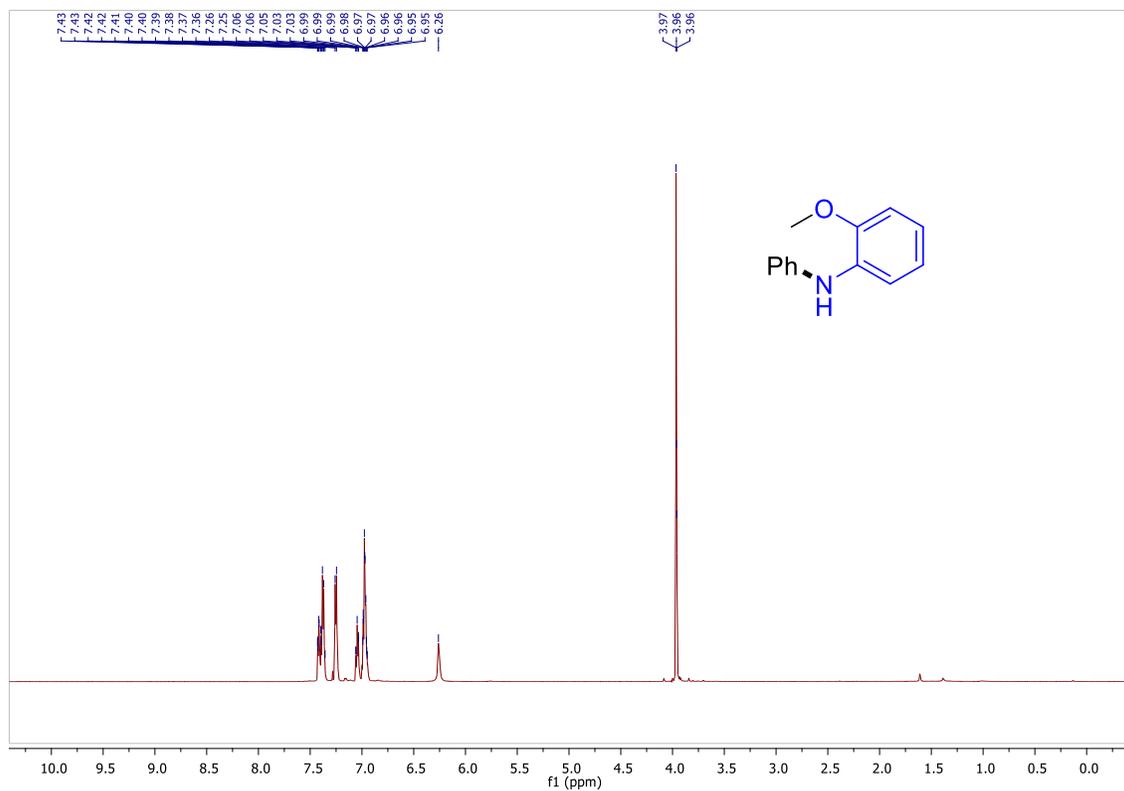
¹H and ¹³C NMR of 3-bromo-N-phenylaniline (4e)



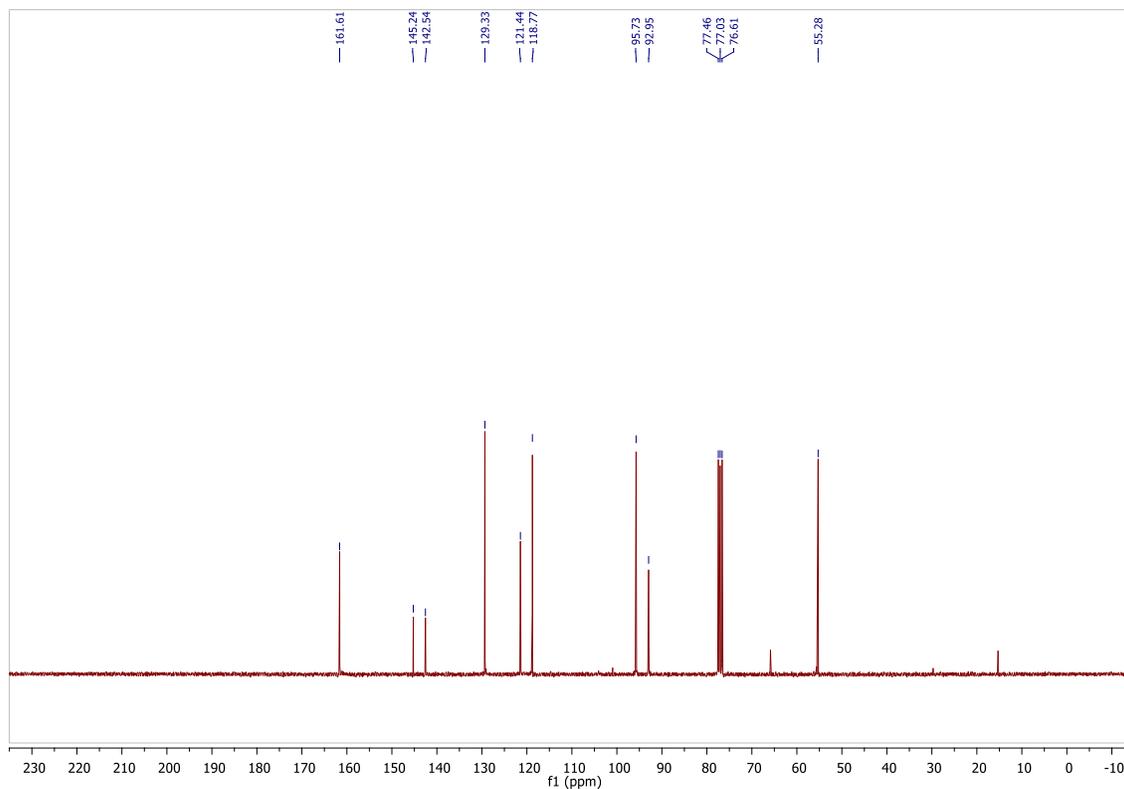
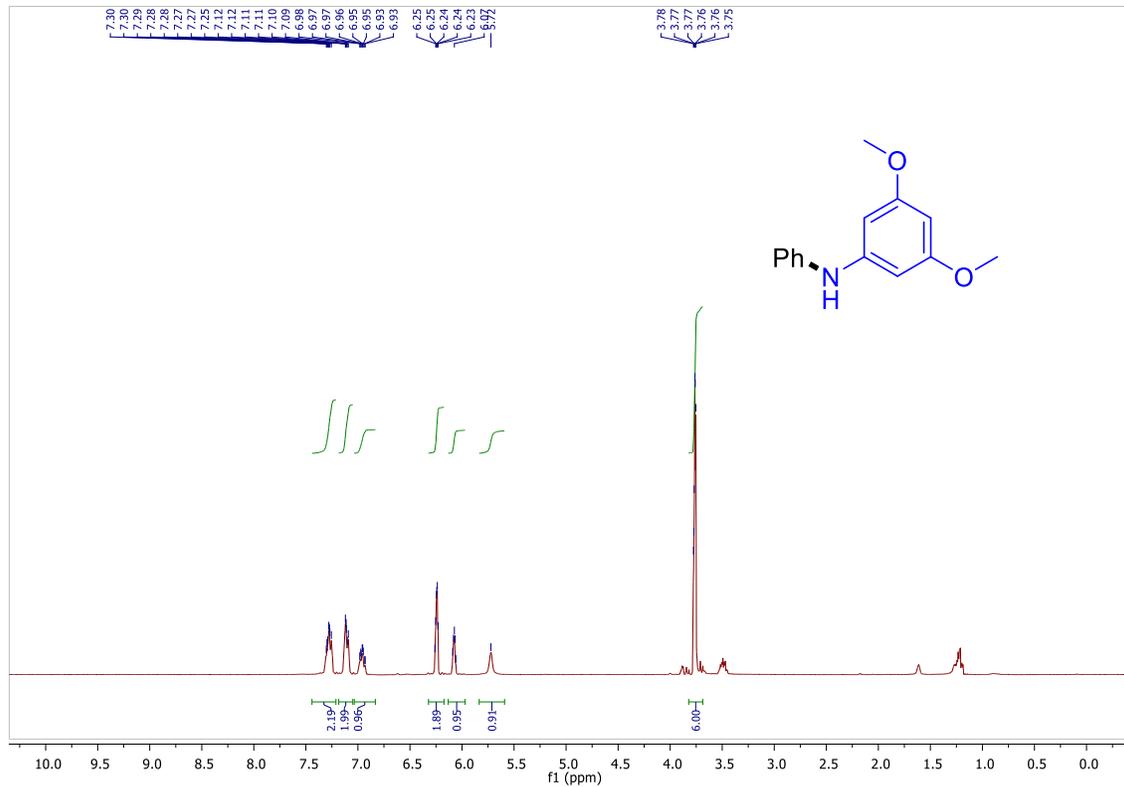
¹H and ¹³C NMR of 2-fluoro-N-phenylaniline (4f)



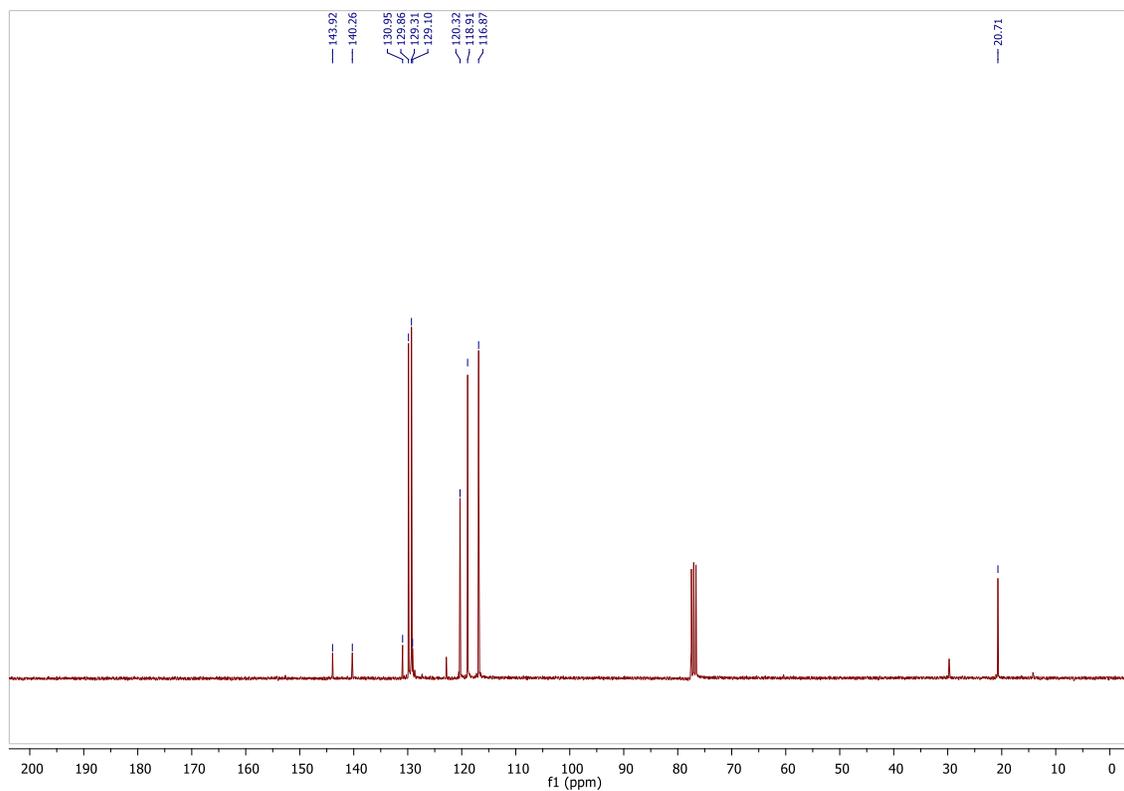
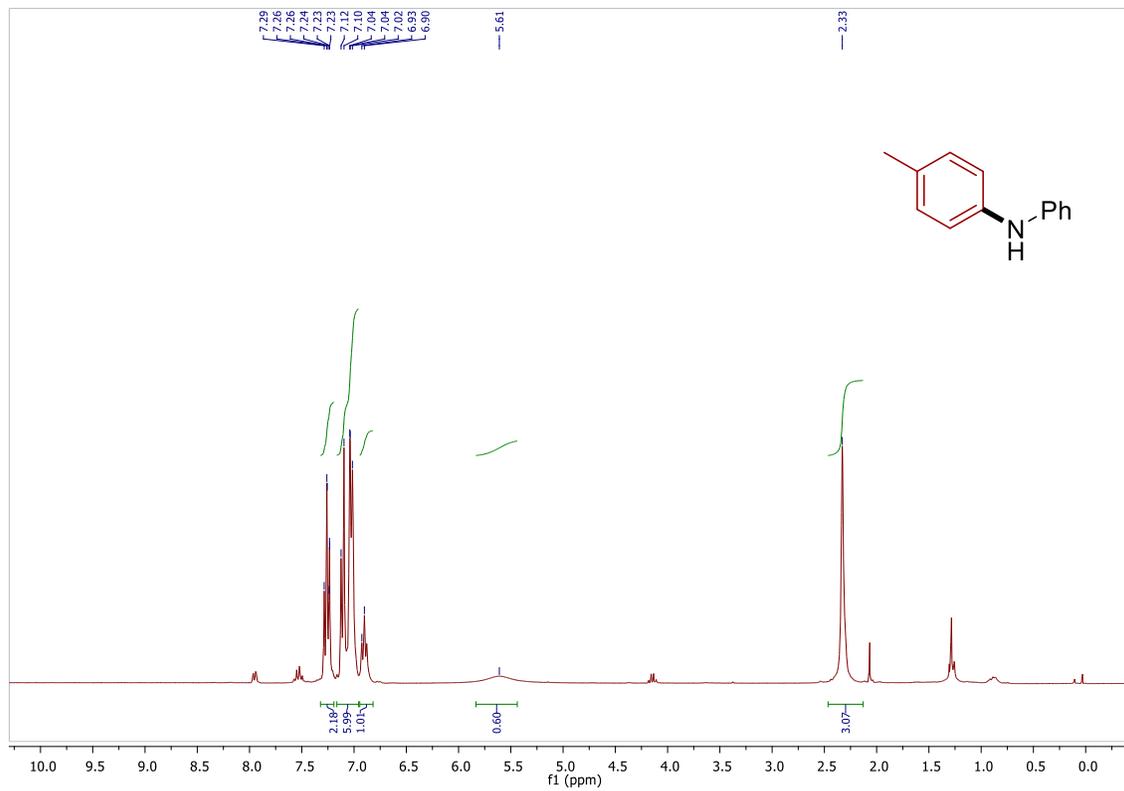
¹H and ¹³C NMR of 2-chloro-N-phenylaniline (4g)



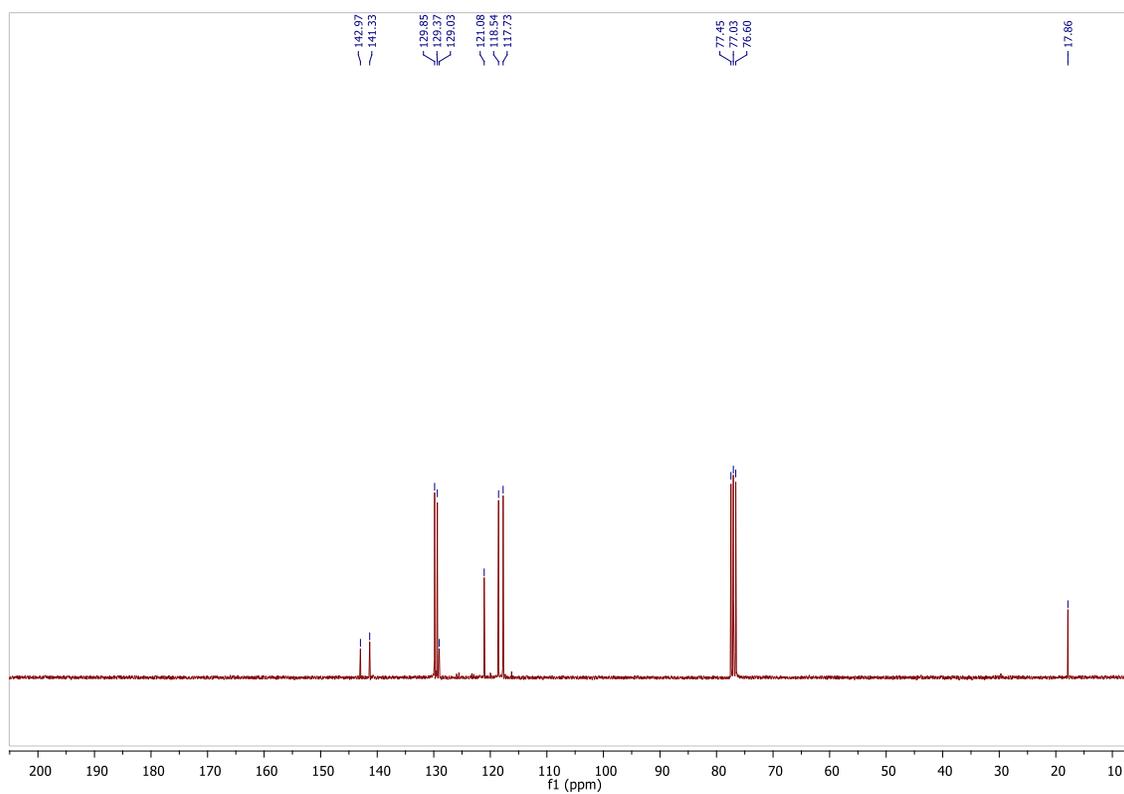
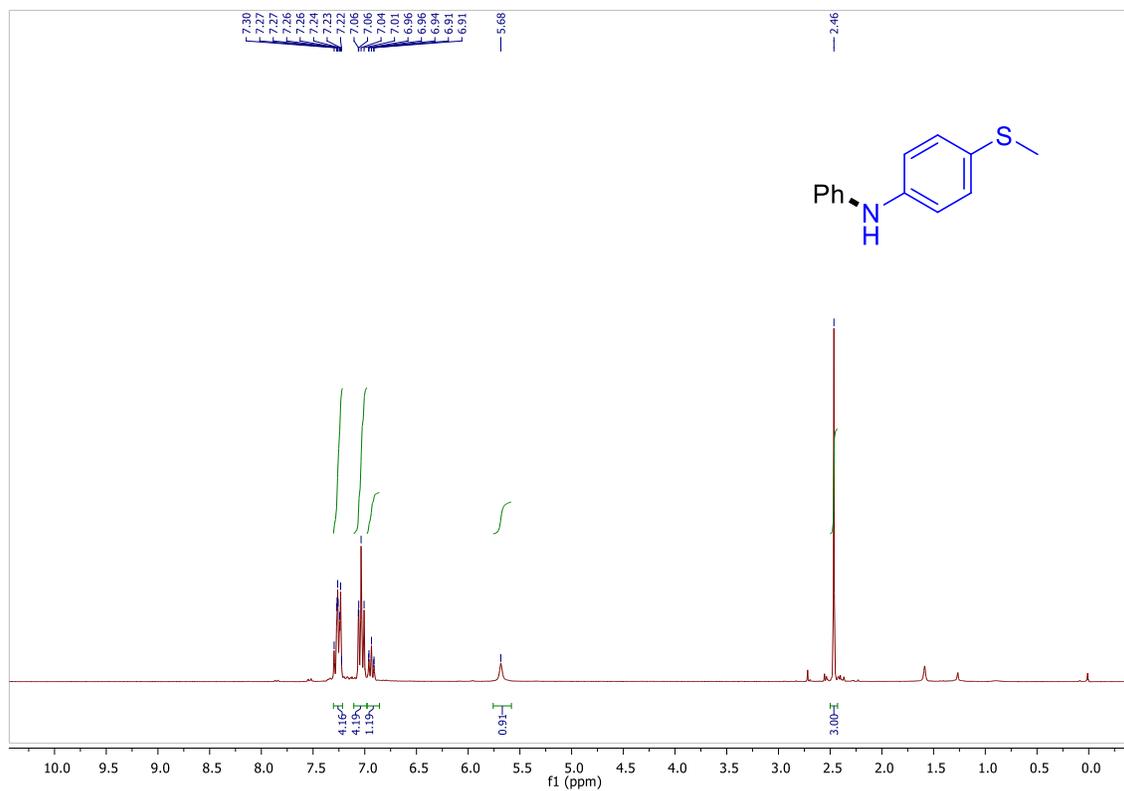
¹H and ¹³C NMR of 2-methoxy-N-phenylaniline (4h)



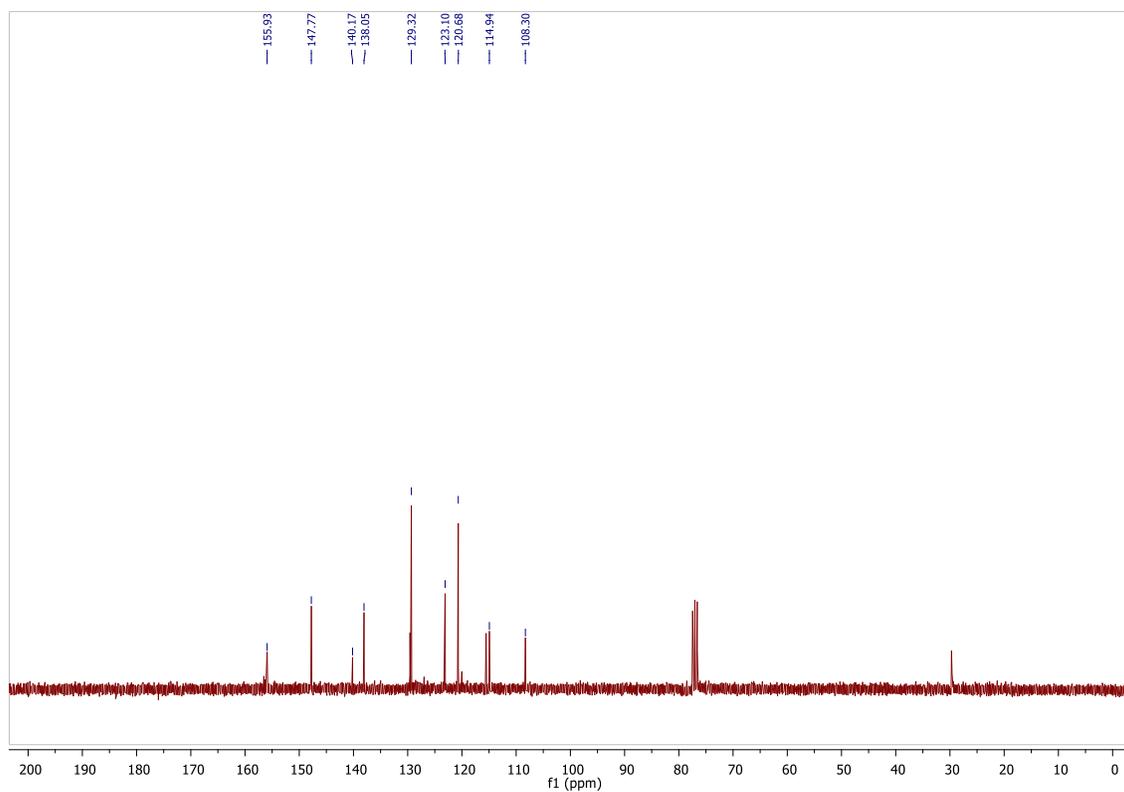
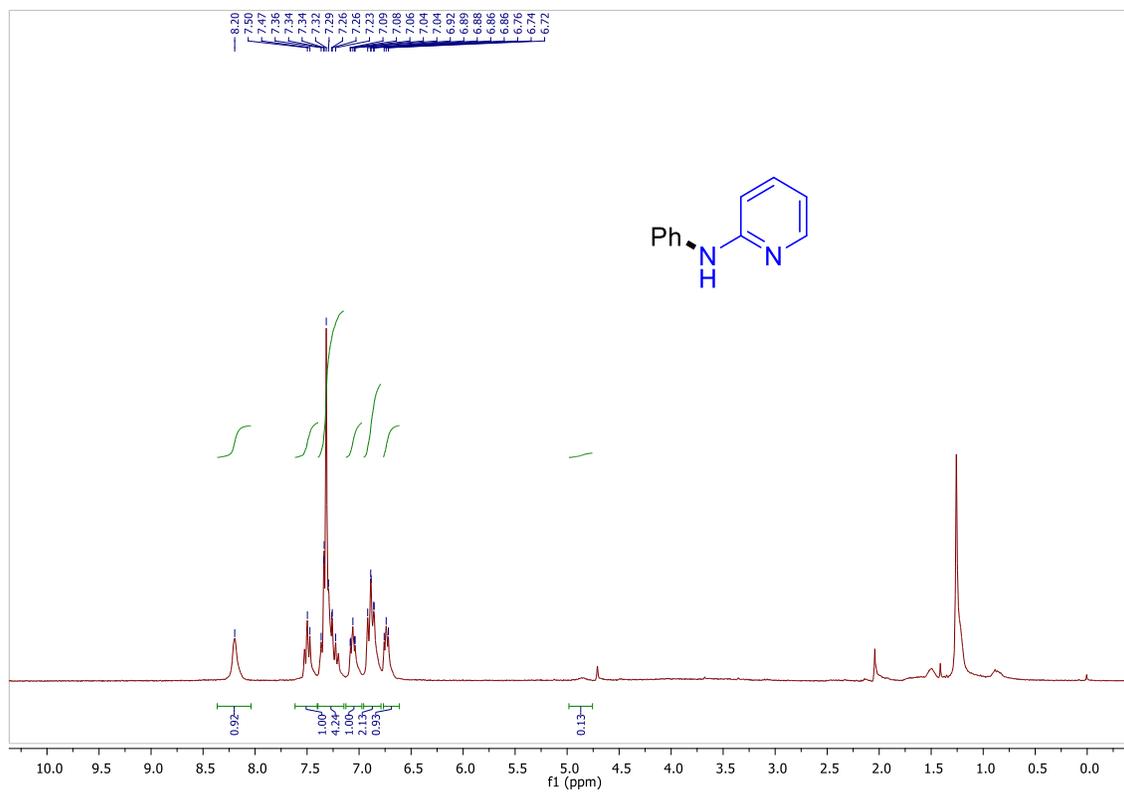
¹H and ¹³C NMR of 3,5-dimethoxy-N-phenylaniline (4i)



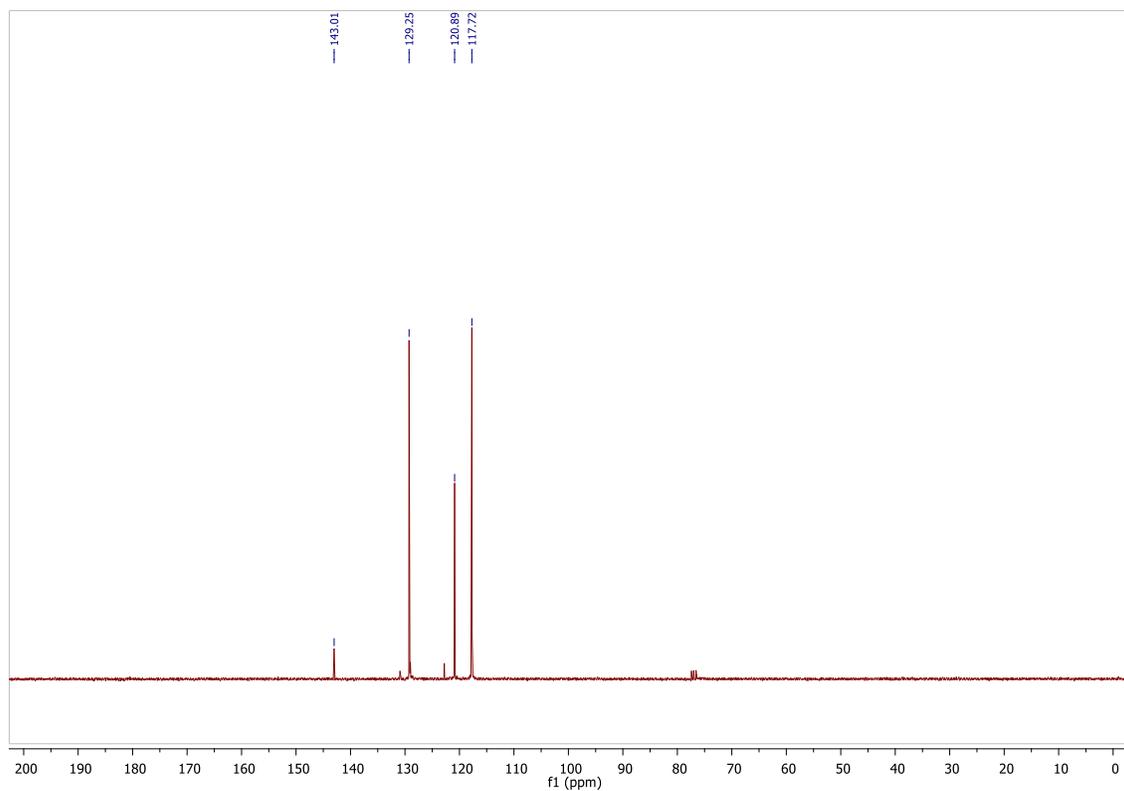
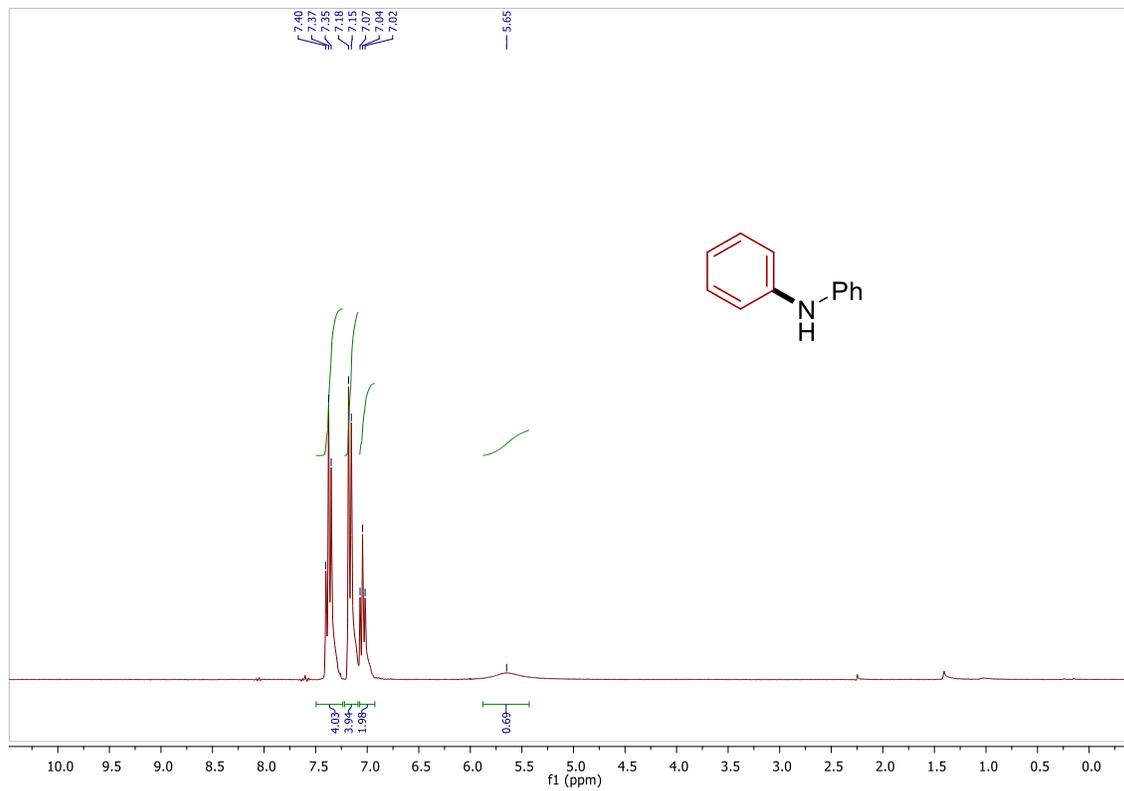
¹H and ¹³C NMR of **4-Methyl-N-phenylaniline (4j)**



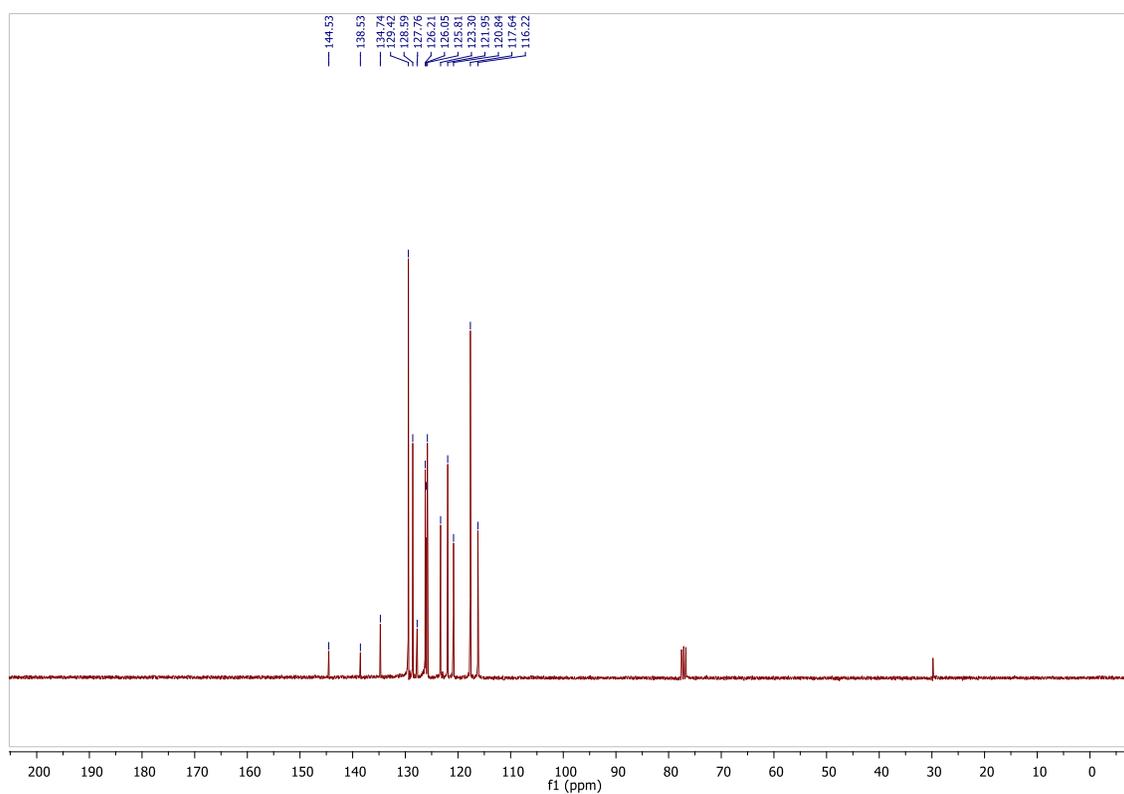
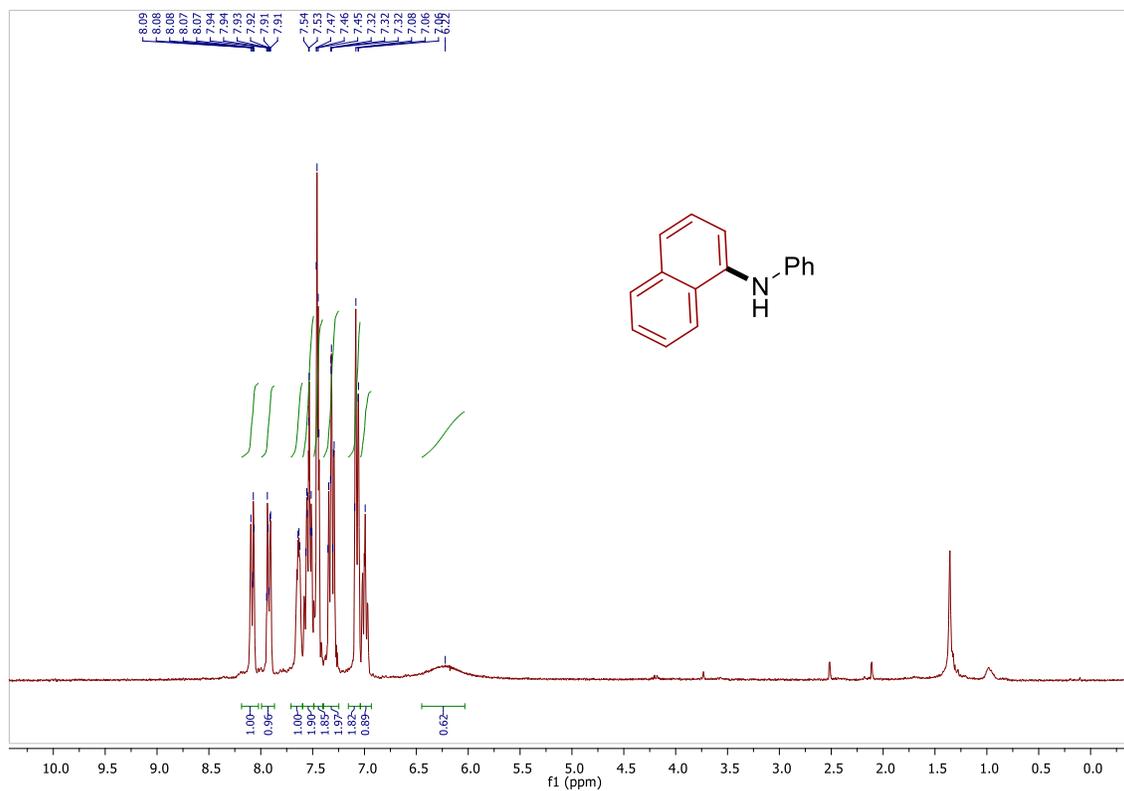
¹H and ¹³C NMR of 4-(methylthio)-N-phenylaniline (4k)



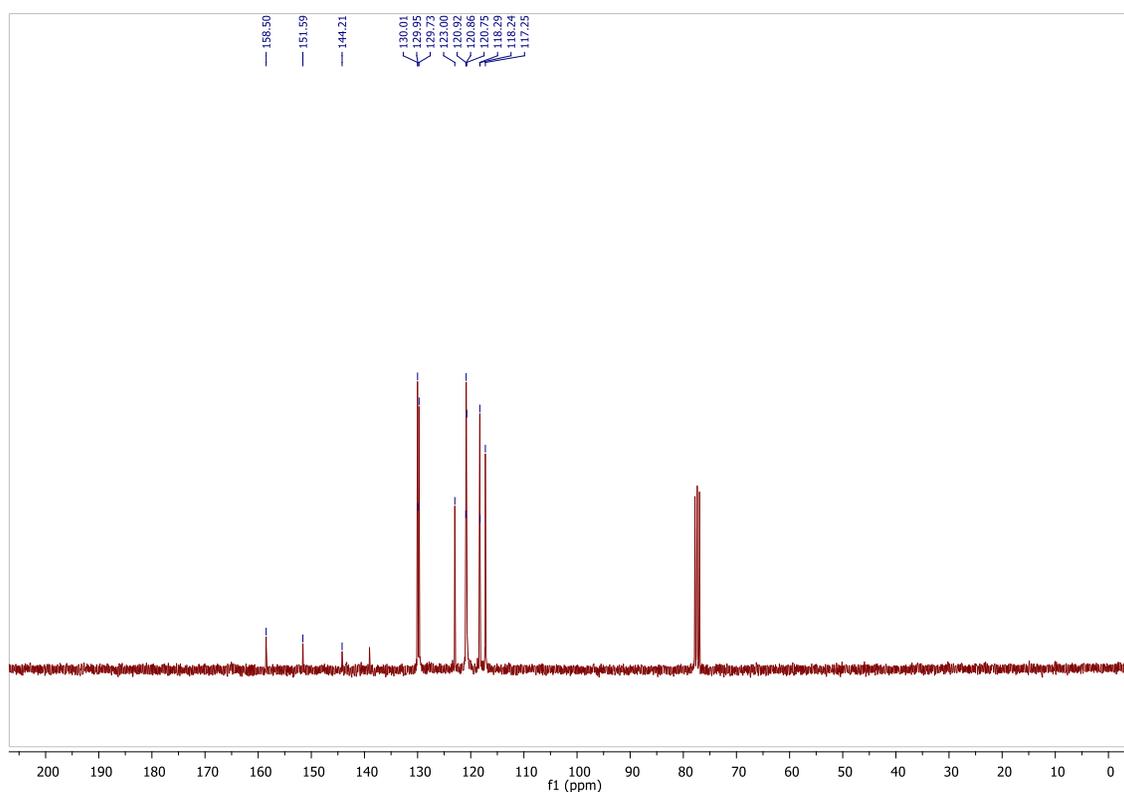
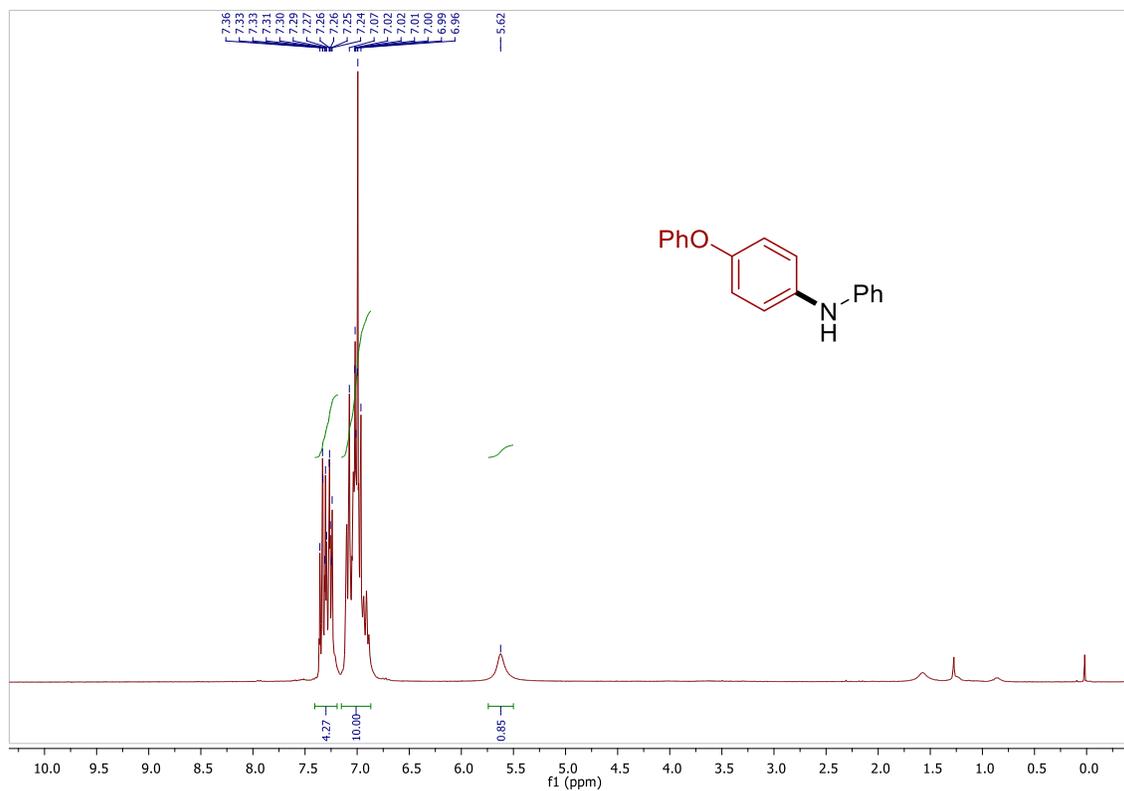
¹H and ¹³C NMR of N-phenylpyridin-2-amine (41)



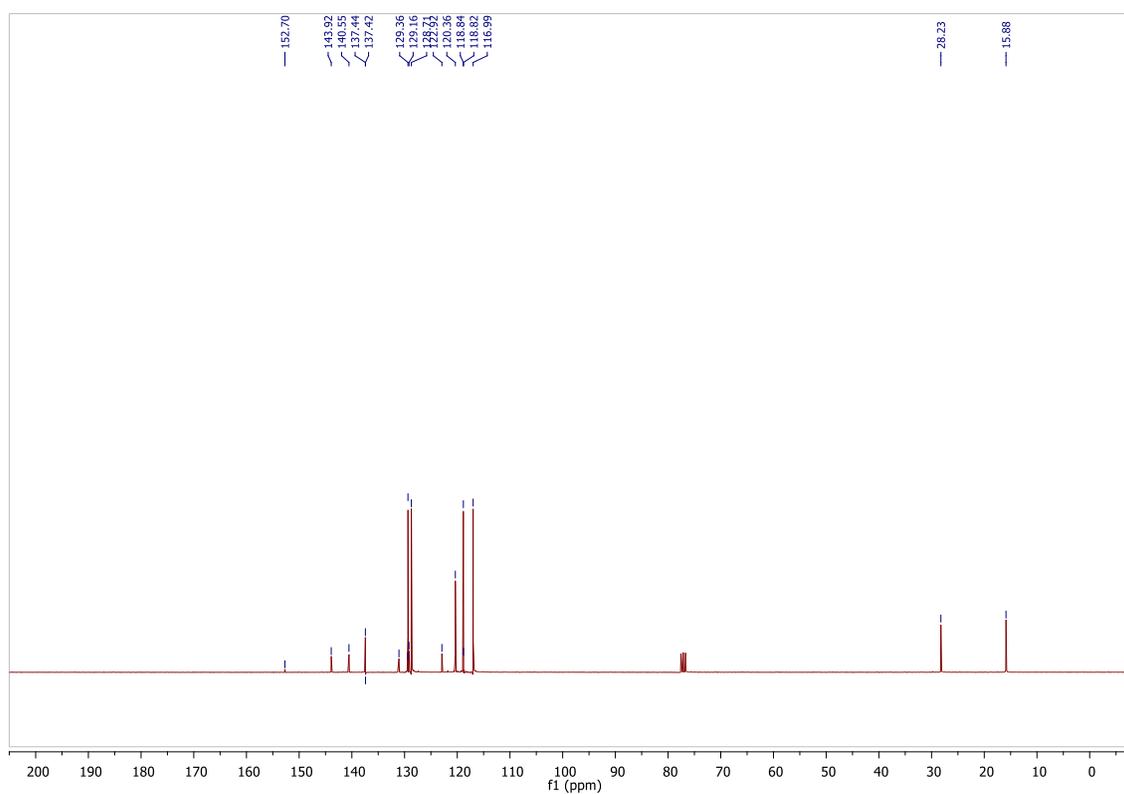
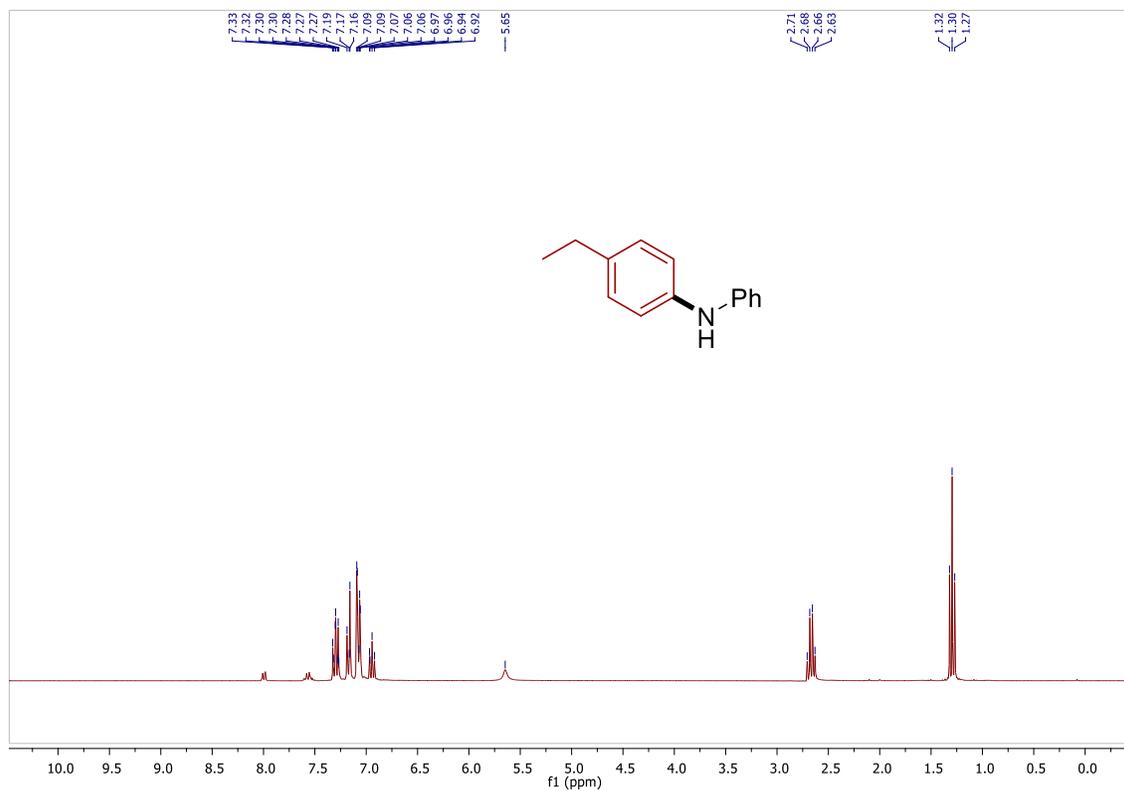
¹H and ¹³C NMR of Diphenylamine (6a)



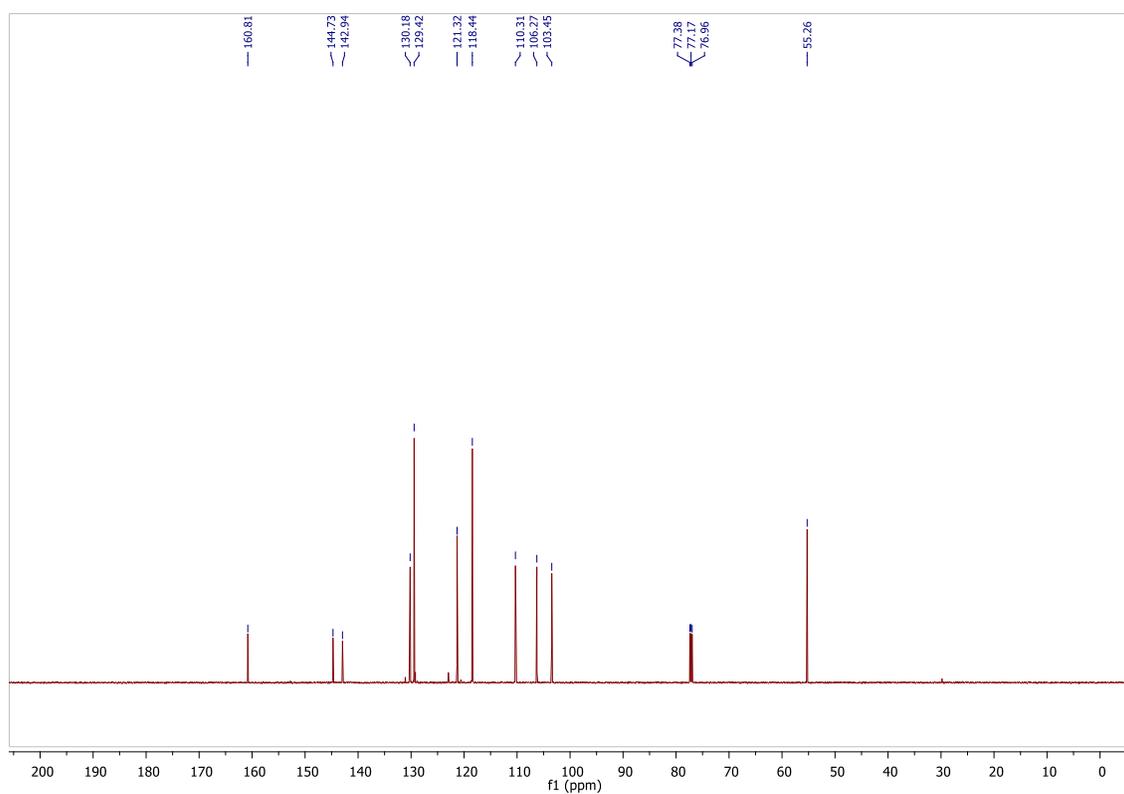
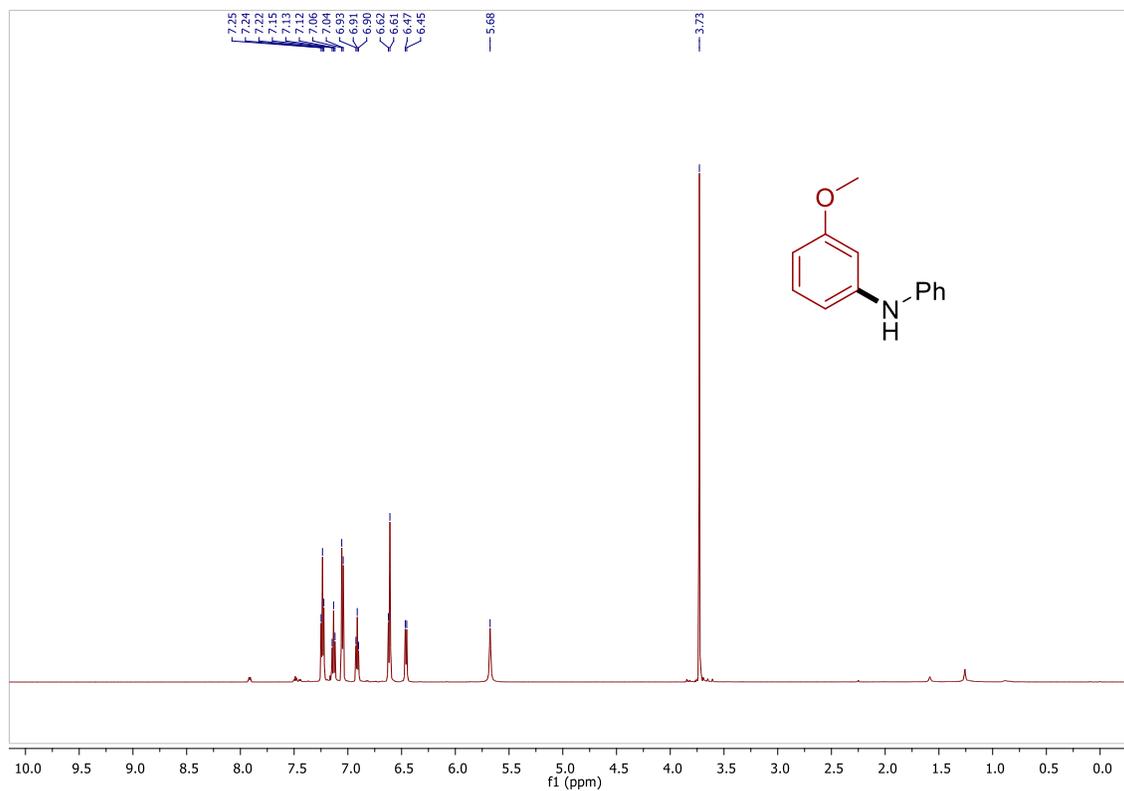
^1H and ^{13}C NMR of N-Phenyl-1-naphthylamine (6b)



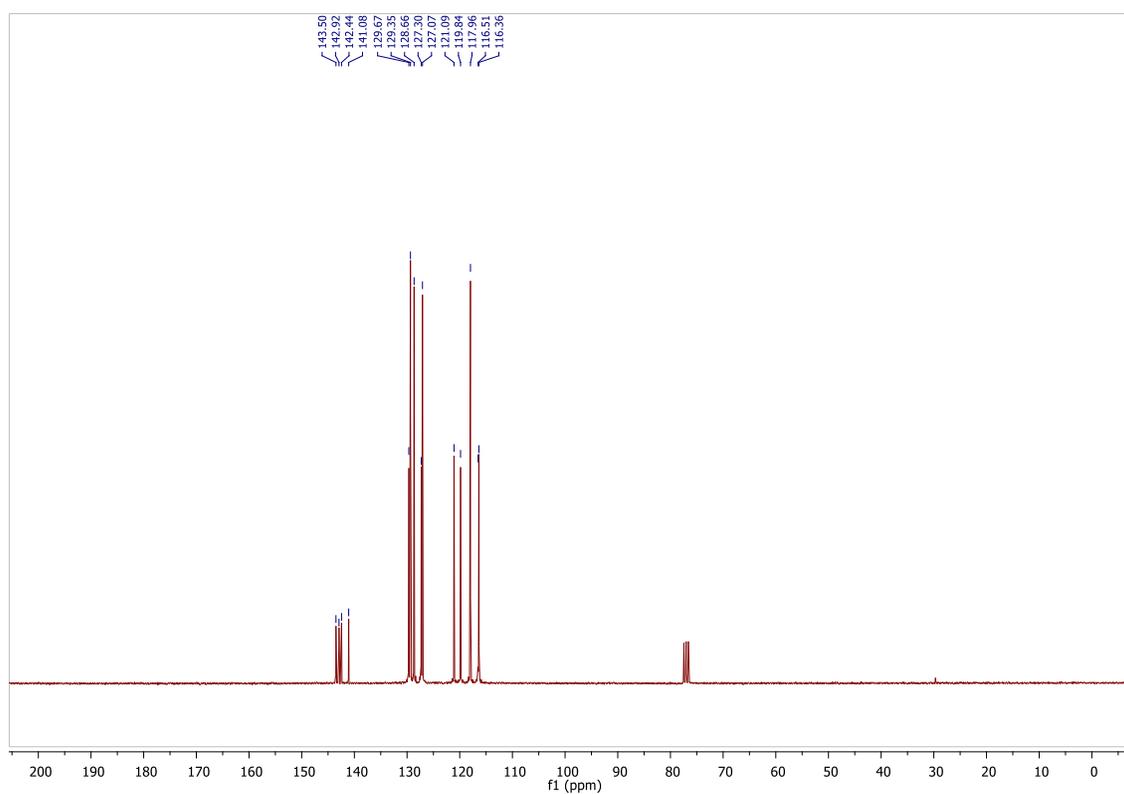
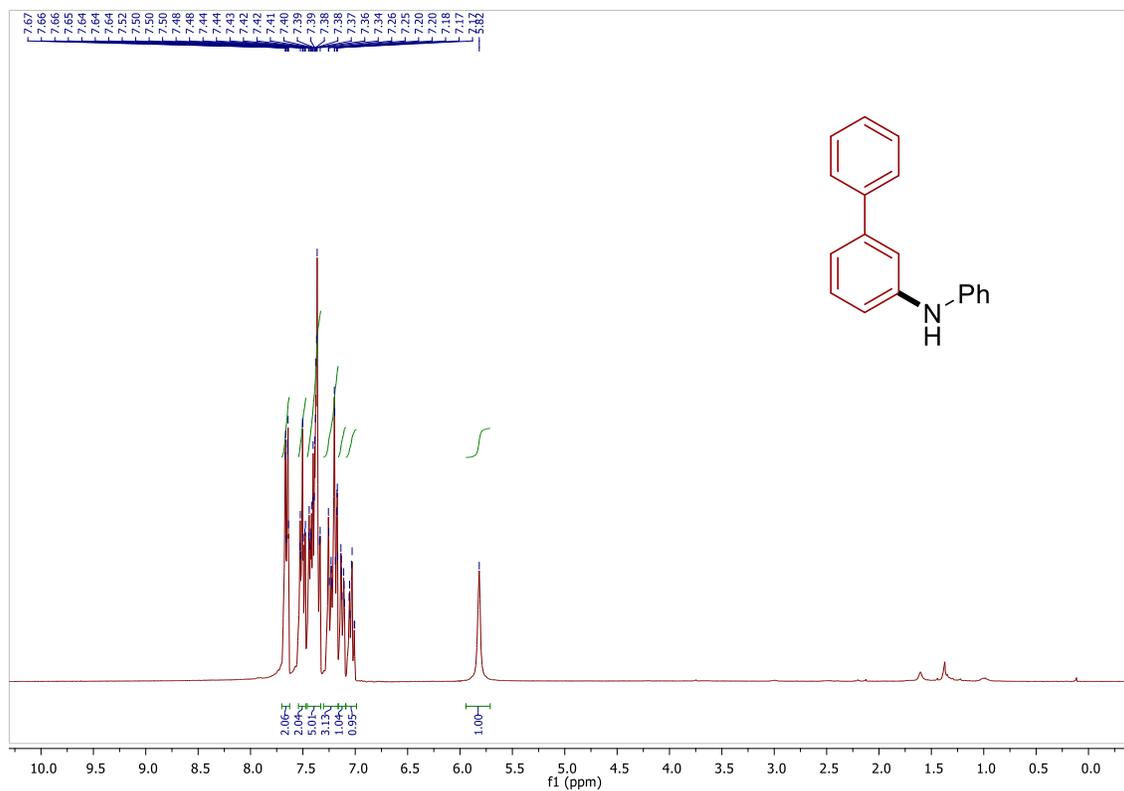
¹H and ¹³C NMR of 4-(Phenoxyphenyl)phenylamine (6c)



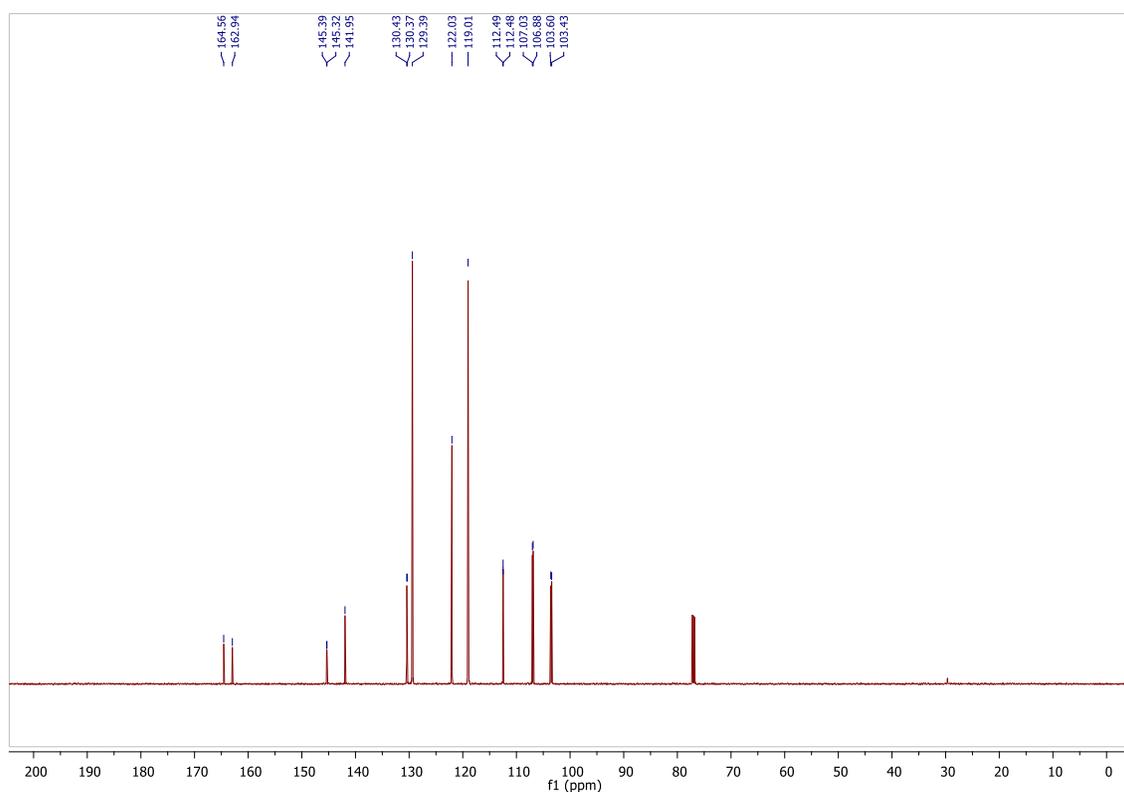
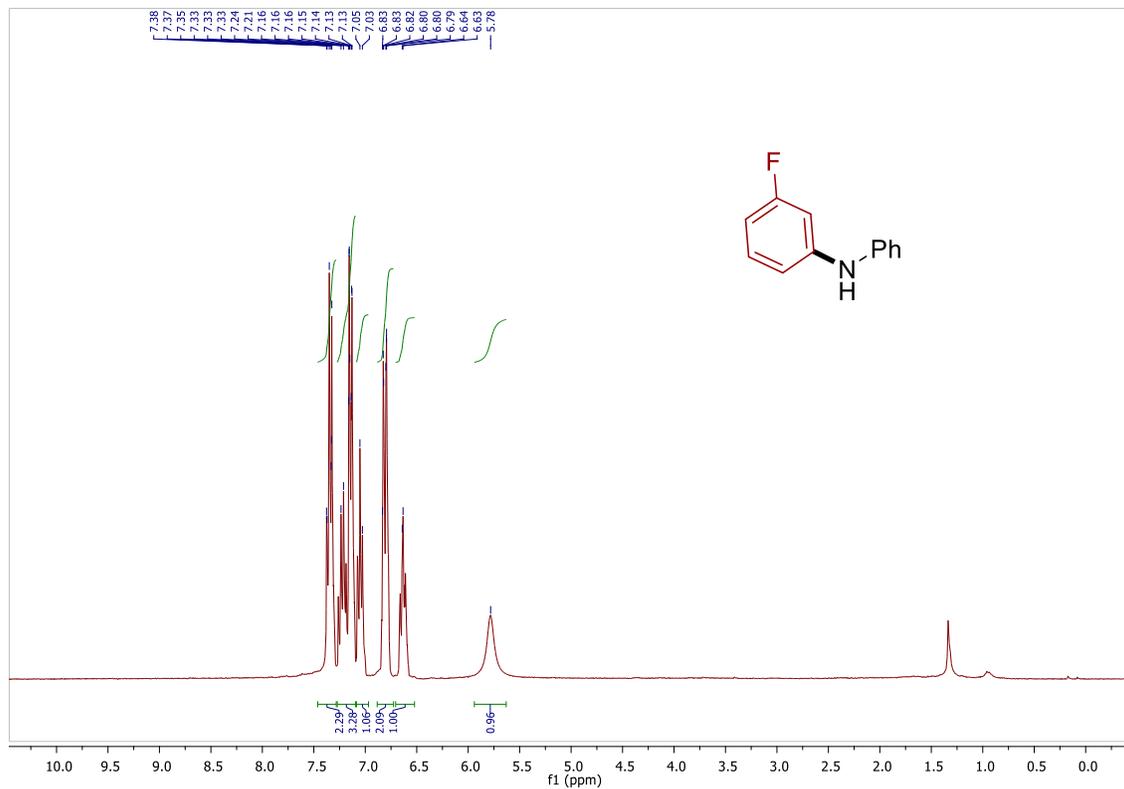
¹H and ¹³C NMR of 4-Ethyl-N-phenylaniline (6d)



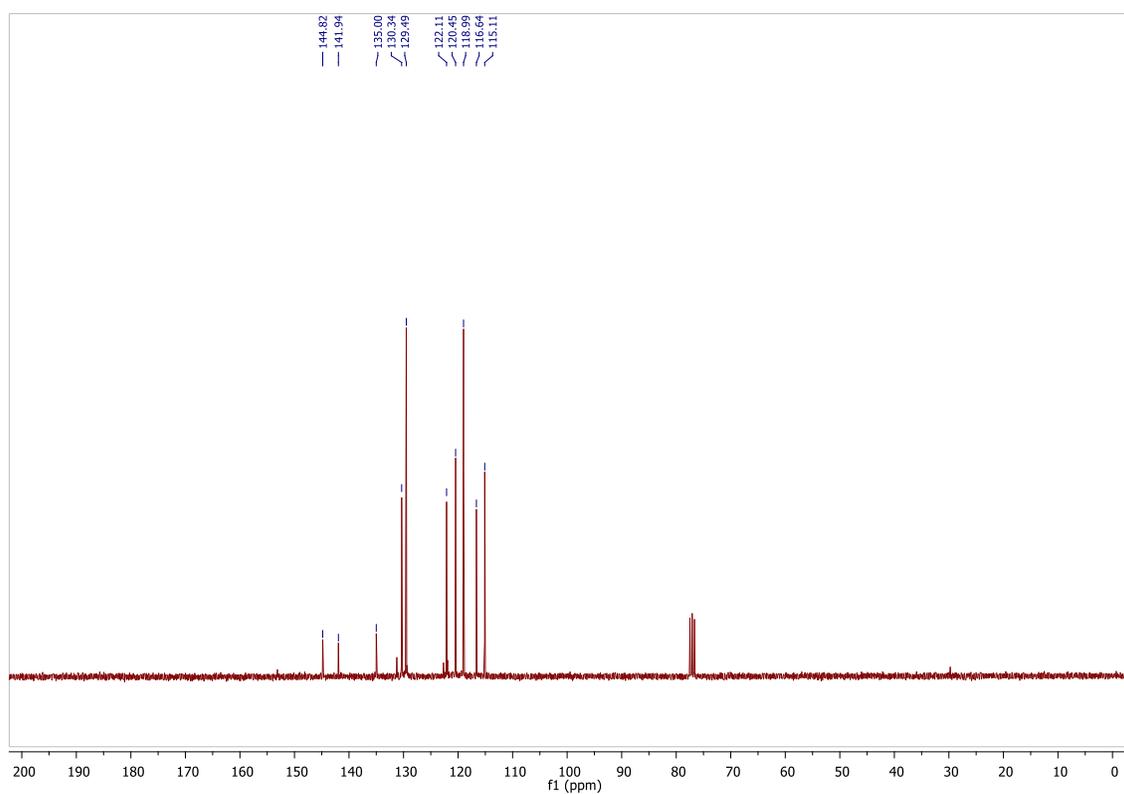
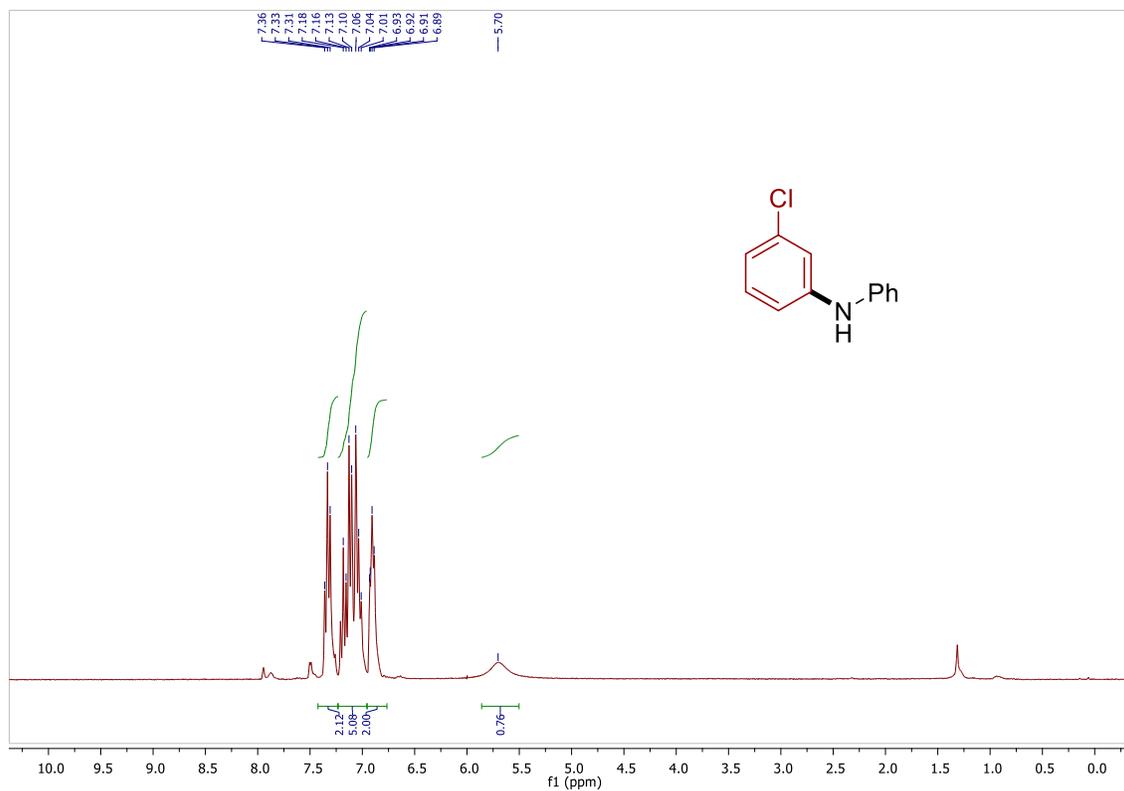
^1H and ^{13}C NMR of **3-Methoxy-N-phenylaniline (6e)**



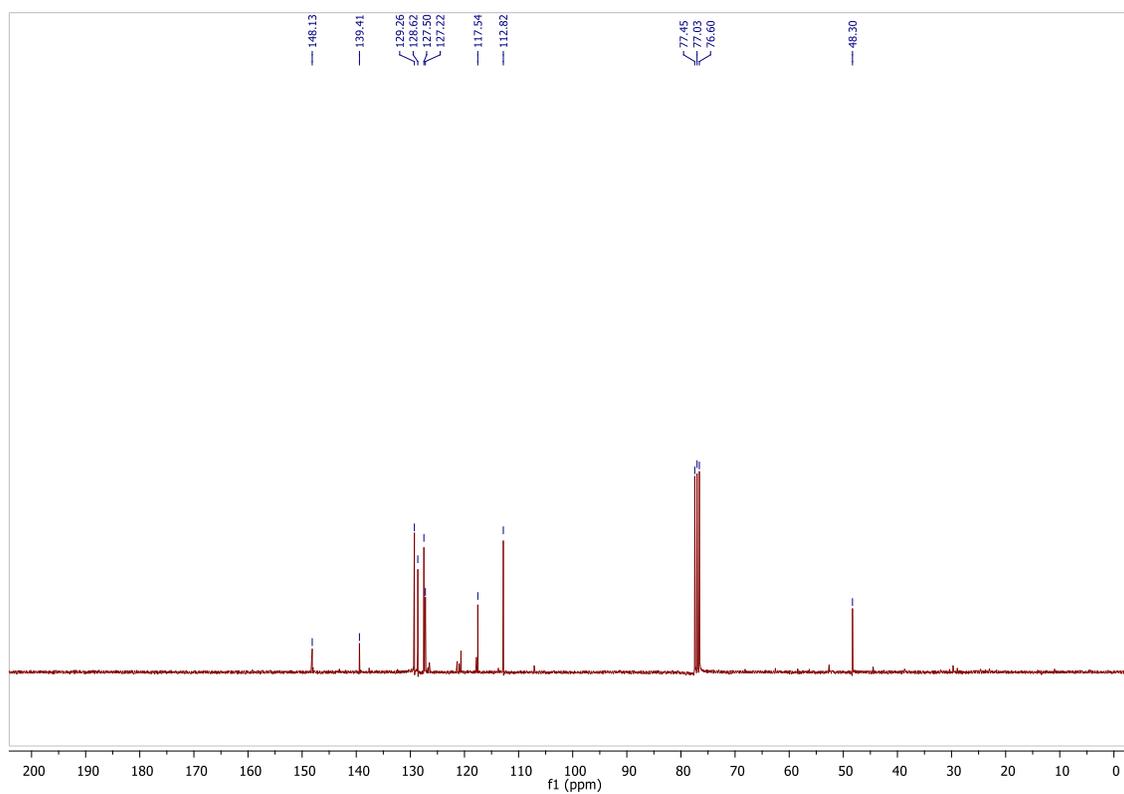
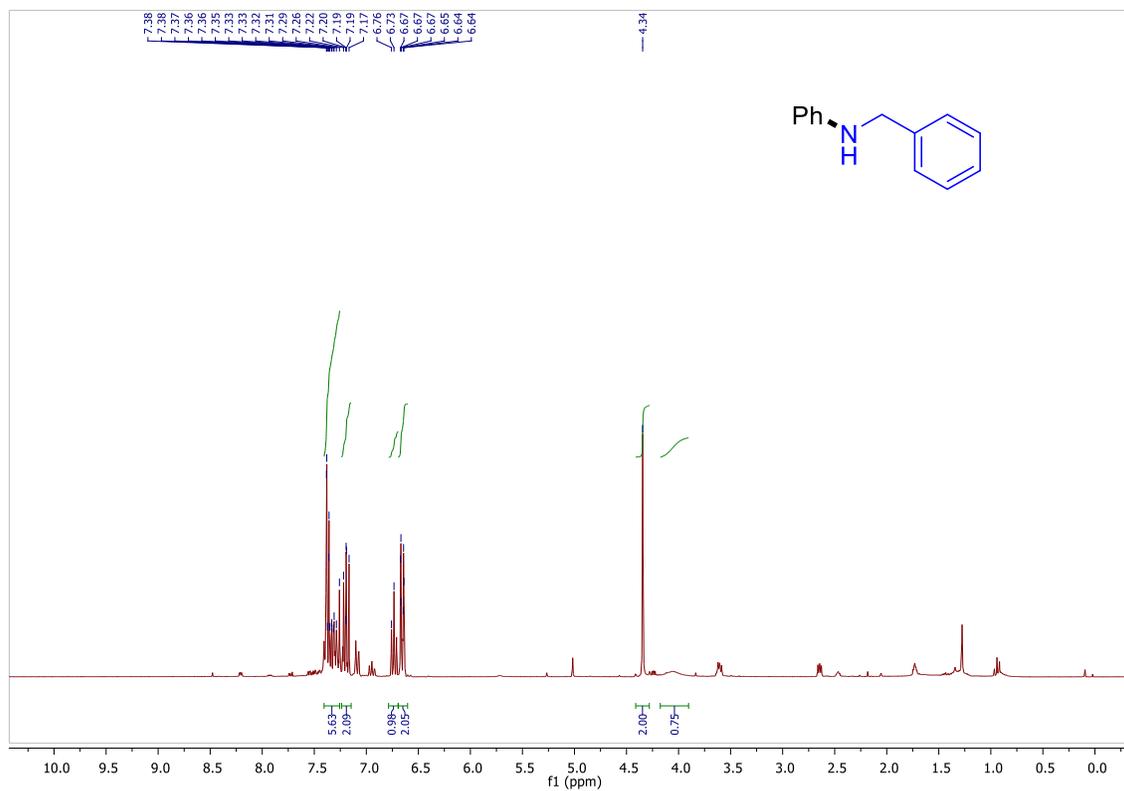
¹H and ¹³C NMR of *N*-(-3-Biphenyl)aniline (**6f**)



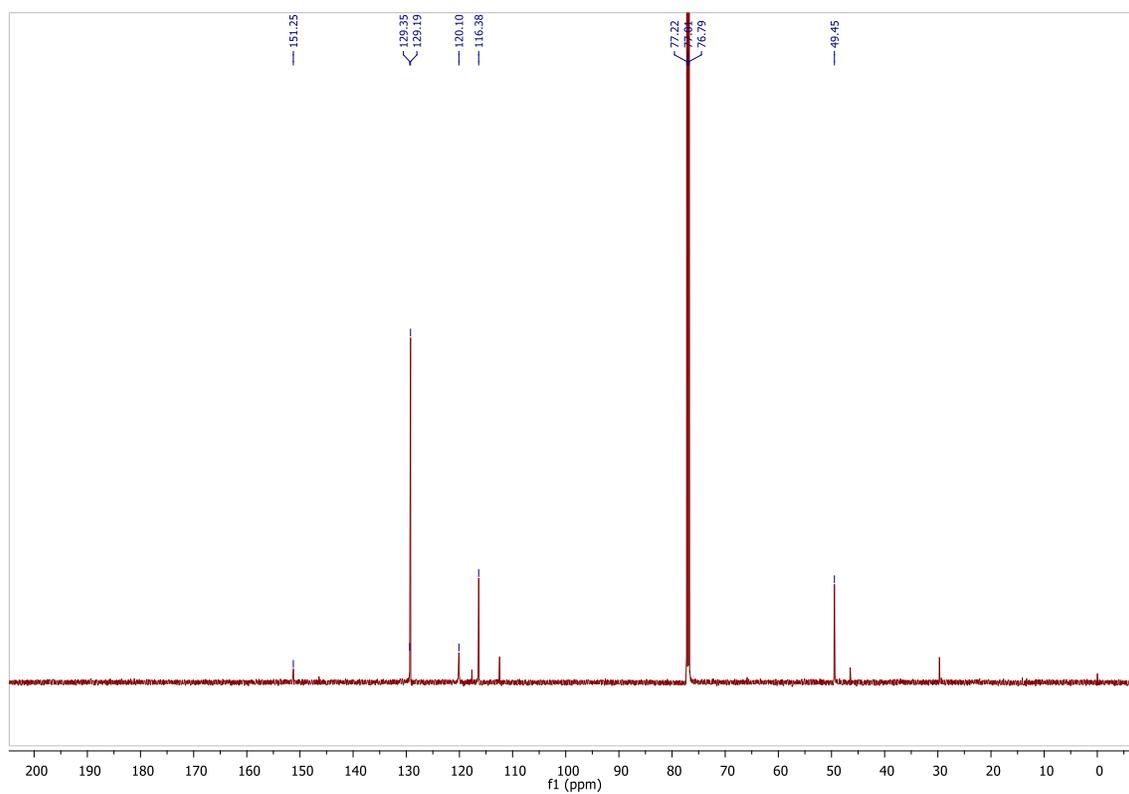
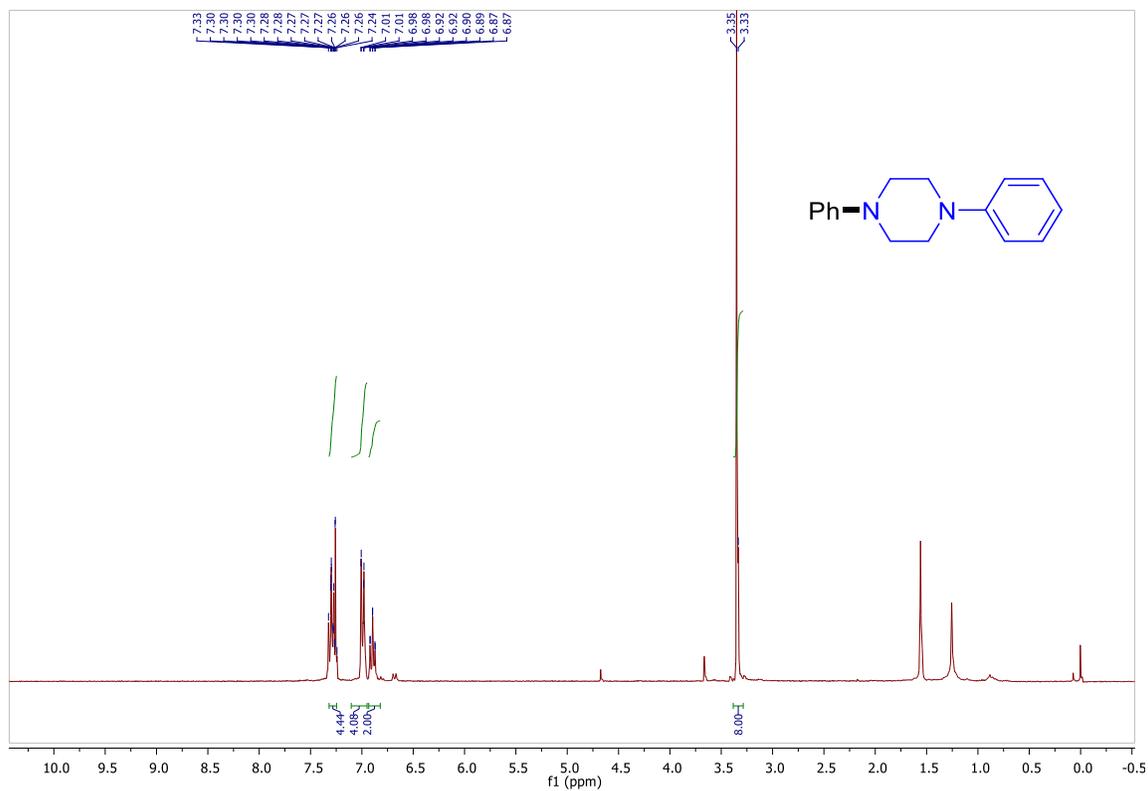
¹H and ¹³C NMR of *N*-(3-Fluorophenyl)-*N*-phenylamine (6g)



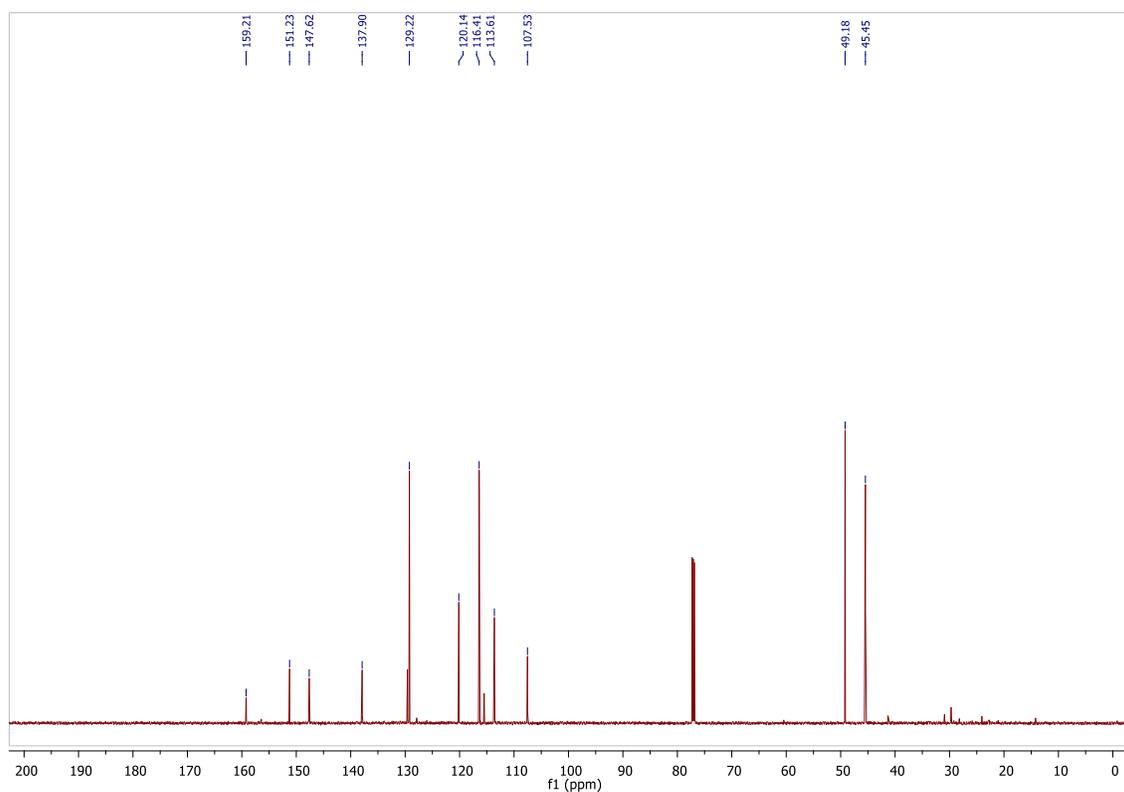
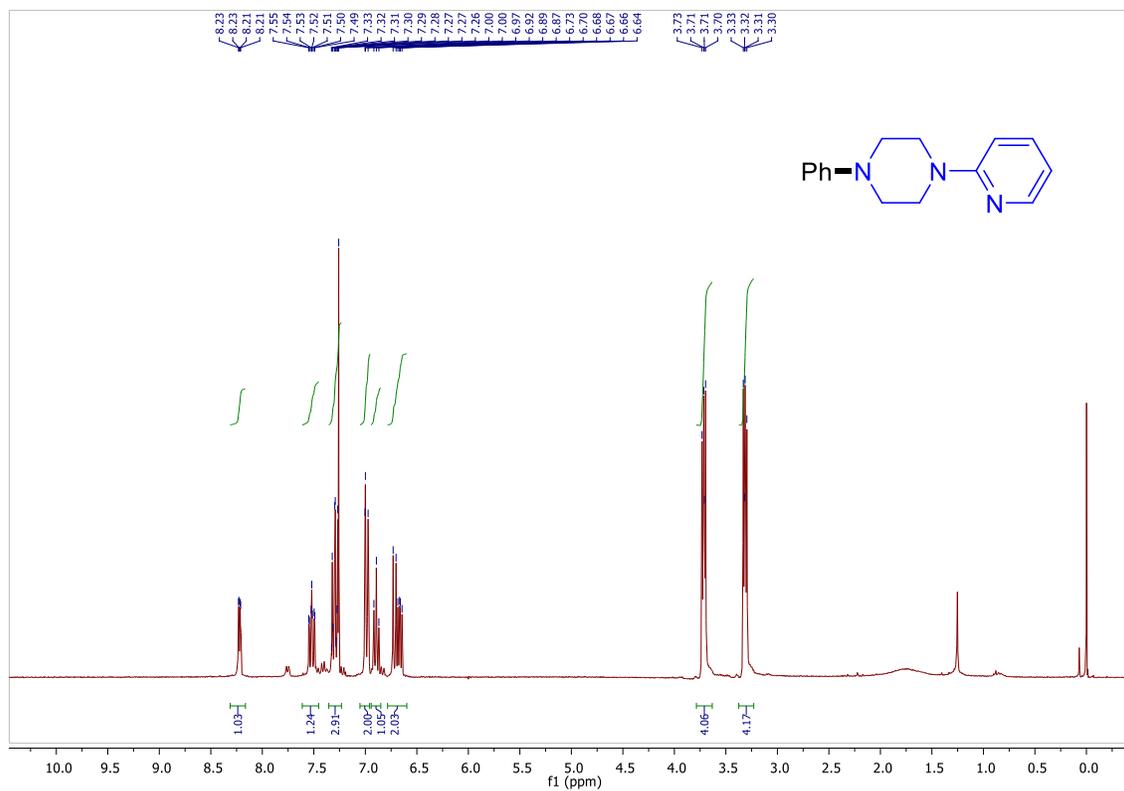
^1H and ^{13}C NMR of 3-Chloro-N-phenylaniline (6h)



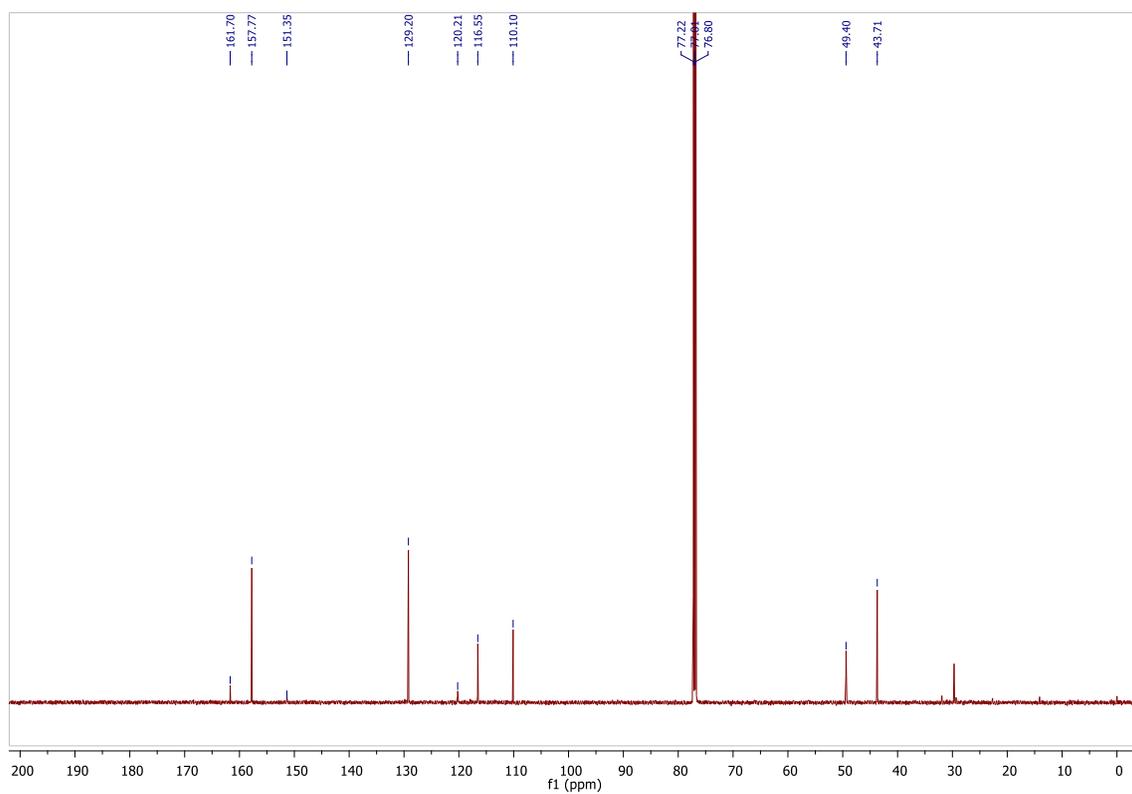
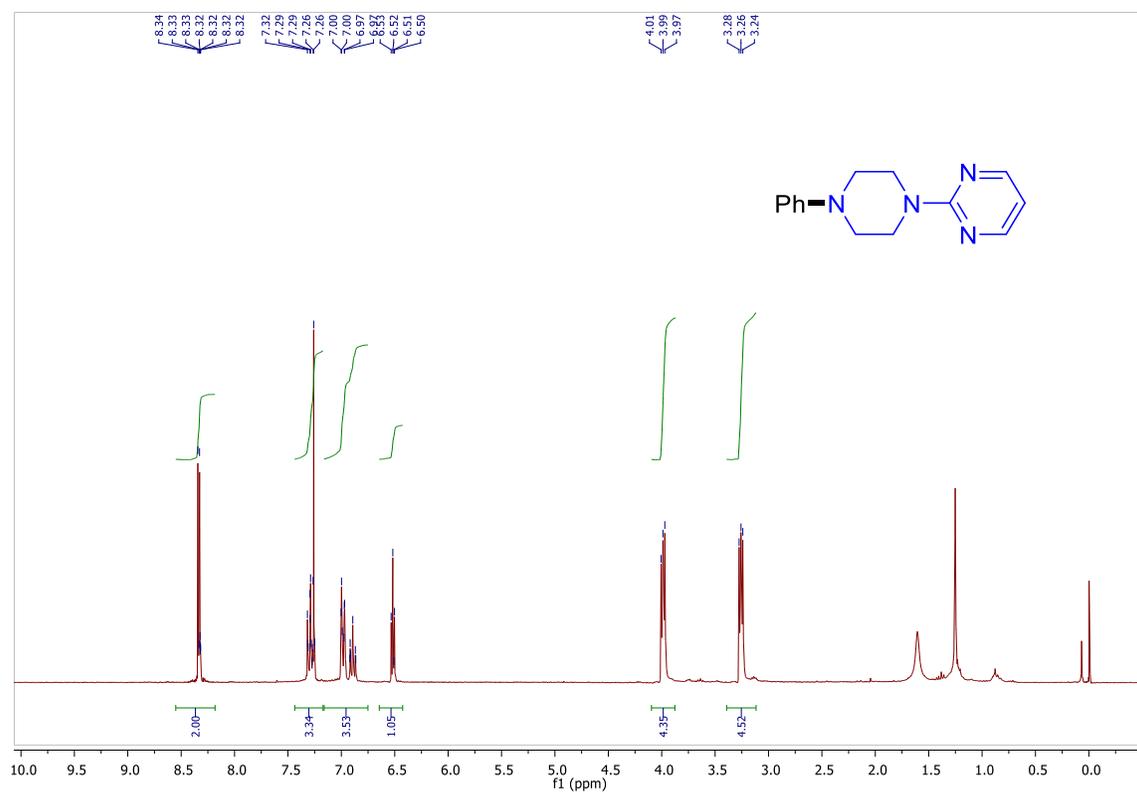
¹H and ¹³C NMR of *N*-benzylaniline (8a)



^1H and ^{13}C NMR of 1,4-Diphenylpiperazine (8b)



¹H and ¹³C NMR of 1-Phenyl-4-(pyridin-2-yl)piperazine (8c)



¹H and ¹³C NMR of 2-(4-Phenylpiperazin-1-yl)pyrimidine (8d)