

Supporting Information

Gold(I)/Zn(II) catalyzed tandem hydroamination/annulation reaction of 4-yne-nitriles

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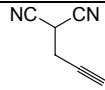
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Materials and Methods.

Chemical shifts δ are reported in ppm relative to CHCl_3 (^1H : δ 7.27 ppm), CDCl_3 (^{13}C : δ 77.0 ppm) and CCl_4 (^{13}C : δ 96.4 ppm) as internal standards. Column chromatography was conducted on silica gel 60 (40–63 μm). Thin-layer chromatography (TLC) was carried out on aluminum sheets pre-coated with silica gel 60F₂₅₄, and the spots were visualized with UV light (λ =254 nm).

Table 3: Cyclization by using (PPh₃)AuCl/ Zn(ClO₄)₂/ (PPh₃)AuCl/ AgSbF₆

entry	Ewg-4	R ² -(5)	Product	yield%	
Zn(ClO ₄) ₂ / AgSbF ₆					
1		Ph-5a	6aa/7aa	65	58
2		3,4-dimethyl-Ph-5b	6ab/7ab	62	41
3		<i>p</i> -MeO-Ph-5c	6ac/7ac	74	46
4	4a (R ¹ =H)	<i>p</i> -Cl-Ph-5e	6ae/7ae	65	51
5		<i>m</i> -Cl-Ph-5f	6af/7af	47	60
6		Benzyl-5g	6ag/7ag	81	40
7		Ethyl-5i	6ai/7ai	56	39
8		Ph-5a	6ba/7ba	67	44
9		3,4-dimethyl-Ph-5b	6bb/6bb	65	41

10		MeO-Ph-5c	6bc/6bc	72	39
11		Benzyl-5g	6bg/7bg	73	44
4b (R ¹ =H)					

Experimental Procedures

General procedure for propargylation of ethylcyanoacetate and malonedinitrile

Method A: NaH (3.6 gr, 0.15 mol) was added slowly to a stirred solution of (ethylcyanoacetate/ malonedinitrile) (5.65 gr/ 3.3 gr, 0.05 mol) in THF at 0 °C under argon. The reaction mixture was stirred for 1 h and then a solution of propargylbromide ((150 ml) 6.49 gr, 0.055 mol) in THF (25 ml) was added dropwise (1 hour) and stirred at room temperature for 8 h. The reaction was monitored by TLC. Water was added, the mixture extracted with ethyl acetate and the combined organic layers were dried over MgSO₄. After the evaporation of the solvent under reduced pressure, the crude product was purified on silica gel to afford **4a/b** (15%/18%) (hexane– ethyl acetate (4–1)).

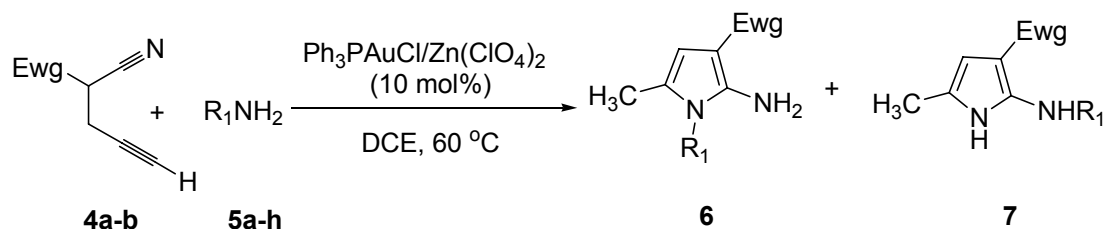
Method B: ^tBuOK (0.15 mol) was added to a stirred solution of (ethylcyanoacetate/ malonedinitrile) (5.65 gr/ 3.30 gr, 0.05 mol) in isopropanol (150 ml) at 0 °C and was stirred for 1 h and then propargylbromide (6.49 gr, 0.055 mol) was added dropwise (2 hours) and stirred for 8h at room temperature. The reaction was monitored by TLC. After the removal of the solvent in vacuo, water was added slowly and the mixture extracted with ethyl acetate. The combined organic layers were dried over MgSO₄. After the evaporation of the solvent under reduced pressure, the crude product was purified on silica gel to afford **4a/b** (17%/20%) (hexane– ethyl acetate (4–1)).

Ethyl 2-cyanopent-4-ynoate (4a)

Colorless oil, ¹H NMR (400 MHz, CDCl₃): δ 1.37 (3H, m), 2.21 (1H, br.s), 2.86 (2H, m), 3.71 (1H, t, *J*=6.6 Hz), 4.31 (2H, m); ¹³C NMR (100 MHz, CDCl₃): 13.9, 20.0, 37.0, 63.3, 72.6, 72.3, 115.2, 164.4. Anal. Calcd for C₈H₉NO₂ (151.16): C, 63.56; H, 6.00; N, 9.27. Found: C, 63.50; H, 6.13; N, 9.24.

2-(Prop-2-ynyl)malononitrile (4b)

Colorless oil, ¹H NMR (400 MHz, CDCl₃): δ 2.40 (1H, t, *J*=2.6 Hz), 2.95 (2H, dd, *J*=2.6 Hz, *J*=6.7 Hz), 3.96 (1H, t, *J*=6.7 Hz); ¹³C NMR (100 MHz, CDCl₃): 21.7, 22.9, 74.8, 75.1, 111.5; Anal. Calcd for C₆H₄N₂ (104.11): C, 69.22; H, 3.87; N, 26.91. Found: C, 69.25; H, 3.88; N, 26.87.



Scheme2: General reaction

General procedure for synthesis of 2-aminopyrroles (6,7)

The catalyst mixture (10 mol% PPh₃AuCl, 10 mol% Zn(ClO₄)₂) was added to a solution of the nitrile-yne **4a,b** (1 mmol) and Amine **5a-h** (1,2 mmol) in DCE (5ml). The resulting mixture was stirred at 60 °C and monitored periodically by TLC. Upon completion of the reaction, water was added, the mixture extracted with ethyl acetate and the combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified on silica gel to afford compound 6 and 7 (Petroleum ether– diethylether (4–1) to (6-1)).

Ethyl 2-amino-5-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (**6aa**)

Yellow oil, IR (neat): 3396, 3304, 2967, 1698, 1551 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.31 (3H, t, *J*=7.1 Hz), 1.92 (3H, s), 4.25 (2H, q, *J*= 7.1 Hz), 4.79 (2H, bs, NH₂), 6.06 (1H, s), 7.10-7.51 (5H, m); ¹³C NMR (100 MHz, CDCl₃): 12.4, 14.7, 58.7, 92.4, 104.3, 121.9, 128.1, 128.6, 129.8, 135.83, 146.3, 165.9. Anal. Calcd for C₁₄H₁₆N₂O₂ (244.3): C, 68.83; H, 6.60; N, 11.47. Found: C, 68.80; H, 6.53; N, 11.39.

Ethyl 5-methyl-2-(phenylamino)-1*H*-pyrrole-3-carboxylate (**7aa**)

Yellow oil, IR (neat): 3387, 3022, 2894, 1681, 1595 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.26 (3H, t, *J*=7.1 Hz), 2.09 (3H, s), 4.16 (2H, q, *J*=7.1 Hz), 5.90 (1H, s), 6.89-7.24 (5H, m), 7.86 (1H, br s, *NH*), 8.03(1H, br s, *NH*); ¹³C NMR (100 MHz, CDCl₃): 12.9, 14.6, 58.9, 94.9, 104.4, 118.6, 119.5, 122.4,

129.8, 140.9, 141.5, 166.0. Anal. Calcd for $C_{14}H_{16}N_2O_2$ (244.3): C, 68.83; H, 6.60; N, 11.47. Found: C, 68.79; H, 6.55; N, 11.37.

Ethyl 2-amino-5-methyl-1-(2,3-dimethylphenyl)-1H-pyrrole-3-carboxylate (6ab)

Colorless oil, IR (neat): 3356, 2988, 1665, 1548 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 1.33 (3H, t, $J=7.1$ Hz), 1.81 (3H, s), 1.92 (3H, s), 2.35 (3H, s), 4.24 (2H, q, $J=7.1$ Hz), 4.64 (2H, br.s, NH_2), 6.06 (1H, s), 7.01-7.24 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 12.1, 13.7, 14.7, 20.3, 58.6, 92.2, 103.7, 121.8, 125.2, 126.5, 128.9, 130.7, 136.0, 138.8, 145.4, 166.0. Anal. Calcd for $C_{16}H_{20}N_2O_2$ (272.2): C, 70.56; H, 7.40; N, 10.29. Found: C, 70.51; H, 7.38; N, 10.24.

Ethyl 2-(2,3-dimethylphenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ab)

Yellow oil, IR (neat): 3396, 3275, 2962, 1621, 1599 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 1.34 (3H, t, $J=7.1$ Hz), 2.14 (3H, s), 2.22 (3H, s), 2.31 (3H, s), 4.24 (2H, q, $J=7.1$ Hz), 5.95 (1H, s), 6.89-7.11 (3H, m), 7.53 (1H, br.s, NH), 7.97 (1H, br s, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 13.0, 13.6, 14.7, 20.7, 58.8, 93.6, 104.1, 117.6, 119.1, 125.5, 128.7, 138.4, 138.7, 143.2, 166.2. Anal. Calcd for $C_{16}H_{20}N_2O_2$ (272.2): C, 70.56; H, 7.40; N, 10.29. Found: C, 70.49; H, 7.36; N, 10.20.

Ethyl 2-amino-1-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carboxylate (6ac)

Yellow oil, IR (neat): 3345, 3267, 2965, 1641, 1556 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 1.25 (3H, t, $J=7.1$ Hz), 1.85 (3H, s), 3.78 (3H, s), 4.17 (2H, q, $J=7.1$ Hz), 4.71 (2H, br.s, NH_2), 5.96 (1H, s), 6.90-7.12 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$): 12.4, 14.7, 55.4, 58.6, 92.1, 103.8, 114.9, 122.3, 128.1, 129.2, 145.8, 159.6, 165.9. Anal. Calcd for $C_{15}H_{18}N_2O_3$ (274.3): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.69; H, 6.63; N, 10.20.

Ethyl 2-(4-methoxyphenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ac)

Yellow oil, IR (neat): 3354, 2974, 1653, 1514 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 1.26 (3H, t, $J=7.1$ Hz), 2.05 (3H, s), 3.72 (3H, s), 4.18 (2H, q, $J=7.1$ Hz), 5.87 (1H, s), 6.71-7.02 (4H, m), 7.45 (1H, br.s, NH), 7.84 (1H, br.s, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 12.0, 14.7, 55.4, 58.8, 104.2, 115.1, 118.9, 122.6, 133.4, 143.7, 156.2, 166.1. Anal. Calcd for $C_{15}H_{18}N_2O_3$ (274.3): C, 65.68; H, 6.61; N, 10.21. Found: C, 65.70; H, 6.60; N, 10.19.

Ethyl 5-methyl-2-(4-nitrophenylamino)-1H-pyrrole-3-carboxylate (7ad)

Dark brown oil, IR (neat): 3326, 2985, 1645, 1531 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.26 (3H, t, $J=7.1$ Hz), 2.19 (3H, s), 4.18 (2H, q, $J=7.1$ Hz), 6.01 (1H, s), 6.91 (2H, d, $J=9.0$ Hz), 8.04 (2H, d, $J=9.0$ Hz), 8.26 (2H, br.s, 2xNH); ^{13}C NMR (100 MHz, CDCl_3): 12.9, 14.5, 59.5, 105.2, 111.2, 112.8, 114.7, 126.2, 140.2, 165.8. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_4$ (289.29): C, 58.13; H, 5.23; N, 14.53. Found: C, 58.09; H, 5.26; N, 14.55.

Ethyl 2-amino-1-(4-chlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (6ae)

Colorless oil, IR (neat): 3419, 3302, 2980, 2359, 1651, 1539 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.26 (3H, t, $J=7.1$ Hz), 1.85 (3H, s), 4.19 (4H, q, $J=7.1$ Hz), 4.72 (2H, br s, NH₂), 6.03 (1H, s), 7.19-7.43 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.4, 14.7, 58.9, 92.7, 104.4, 122.2, 129.4, 130.1, 134.1, 134.8, 145.4, 166.0. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_2$ (278.08): C, 60.33; H, 5.42; N, 10.05. Found: C, 60.31; H, 5.41; N, 10.04.

Ethyl 2-(4-chlorophenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ae)

Yellow oil, IR (neat): 3373, 2979, 2338, 1660, 1597 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.21 (3H, t, $J=7.1$ Hz), 2.06 (3H, s), 4.11 (2H, q, $J=7.1$ Hz), 5.91 (1H, s), 6.82-7.12 (4H, m), 7.84 (1H, br s, NH), 8.07 (1H, br s, NH); ^{13}C NMR (100 MHz, CDCl_3): 12.8, 14.5, 59.2, 95.9, 104.4, 119.4, 120.6, 127.1, 129.7, 139.8, 140.6, 166.2. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_2$ (278.08): C, 60.33; H, 5.42; N, 10.05. Found: C, 60.32; H, 5.40; N, 10.01.

Ethyl 2-amino-1-(3-chlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (6af)

Colorless oil, IR (neat): 3320, 2924, 1696, 1591, 1450 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.27 (3H, t, $J=7.1$ Hz), 1.88 (3H, s), 4.16 (2H, q, $J=7.1$ Hz), 4.73 (2H, br s, NH₂), 5.98 (1H, s), 7.12-7.40 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.5, 14.7, 58.7, 92.8, 96.1, 105.0, 121.5, 126.3, 128.4, 128.9, 130.6, 135.5, 137.1, 145.2, 165.7. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_2$ (278.08): C, 60.33; H, 5.42; N, 10.05. Found: C, 60.32; H, 5.41; N, 10.03.

Ethyl 2-(3-chlorophenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7af)

Oil, IR (neat): 3353, 2998, 2468, 1695, 1587 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.30 (3H, t, $J=7.1$ Hz), 2.19 (3H, s), 4.22 (2H, q, $J=7.1$ Hz), 5.97 (1H, s), 6.89-7.25 (4H, m), 7.91 (1H, br s, NH), 8.08 (1H, br s, NH); ^{13}C NMR (100 MHz, CDCl_3): 12.9, 14.5, 59.0, 96.5, 104.7, 115.8, 117.5, 120.1, 121.9, 130.6, 135.5, 139.8, 142.6, 165.8. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_2$ (278.08): C, 60.33; H, 5.42; N, 10.05. Found: C, 60.29; H, 5.38; N, 10.01.

Ethyl 2-amino-1-benzyl-5-methyl-1H-pyrrole-3-carboxylate (6ag)

Brown oil, IR (neat): 3321, 2948, 1672, 1489 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.35 (3H, t, $J=7.1$ Hz), 2.11 (3H, s), 4.16 (2H, q, $J=7.1$ Hz), 4.63 (2H, br s, NH_2), 4.90 (2H, s), 6.02 (1H, s), 7.33-7.02 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.0, 14.7, 45.4, 58.6, 93.9, 104.1, 121.4, 125.6, 127.5, 128.9, 136.4, 144.9, 165.8. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$ (258.14): C, 69.74; H, 7.02; N, 10.84. Found: C, 69.68; H, 6.98; N, 10.76.

Ethyl 2-(benzylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ag)

Yellow oil, IR (neat): 3352, 2945, 1618, 1512 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.21 (3H, t, $J=7.1$ Hz), 1.95 (3H, s), 4.12 (2H, q, $J=7.1$ Hz), 4.28 (2H, d, $J=5.8$ Hz), 5.79 (1H, s), 6.50 (1H, br.s, NH), 7.20-7.25 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.8, 14.7, 47.9, 58.6, 92.0, 103.9, 119.5, 126.9, 127.5, 128.8, 138.4, 147.7, 166.3. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_2$ (258.14): C, 69.74; H, 7.02; N, 10.84. Found: C, 69.56; H, 6.96; N, 10.70.

2-Amino-5-methyl-1-phenyl-1H-pyrrole-3-carbonitrile (6ba)

Yellow oil, IR (neat): 3393, 3314, 2980, 2230, 1574 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): 1.87 (3H, s), 3.73 (2H, s, NH_2), 5.72 (1H, s), 7.21-7.49 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): 10.3, 103.2, 115.3, 121.0, 125.9, 127.0, 127.8, 133.2, 142.9, 152.2. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3$ (197.24): C, 73.07; H, 5.62; N, 21.30. Found: 73.10; H, 5.64; N, 21.27.

5-Methyl-2-(phenylamino)-1H-pyrrole-3-carbonitrile (7ba)

Colorless oil, IR (neat): 3382, 3323, 2967, 2234, 1485 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.12 (3H, s), 5.89 (1H, br.s, NH), 5.90 (1H, s), 6.75-7.19 (5H, m), 8.01 (1H, br.s, NH); ^{13}C NMR (100 MHz, CDCl_3): 11.0, 105.0, 114.2, 114.8, 119.1, 121.5, 124.8, 127.9, 136.7, 141.2. Anal. Calcd for $\text{C}_{12}\text{H}_{11}\text{N}_3$ (197.24): C, 73.07; H, 5.62; N, 21.30. Found: 73.10; H, 5.60; N, 21.28.

2-Amino-1-(2,3-dimethylphenyl)-5-methyl-1H-pyrrole-3-carbonitrile (6bb)

Yellow oil, IR (neat): 3398, 3329, 2954, 2256, 1512 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.74 (3H, s), 1.83 (3H, s), 2.29 (3H, s), 3.67 (2H, bs, NH_2), 5.84 (1H, s), 6.96-7.20 (3H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.4, 14.1, 20.6, 105.3, 123.3, 126.6, 127.0, 131.5, 134.3, 136.2, 139.4, 142.4, 145.4. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3$ (225.29): C, 74.64; H, 6.71; N, 18.65. Found: 74.67; H, 6.68; N, 18.61.

2-Amino-1-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carbonitrile (6bc)

Yellow oil, IR (neat): 3389, 3312, 2945, 2253, 1523 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): 1.82 (3H, s), 3.79 (2H, bs, NH_2), 3.81 (3H, s), 5.81 (1H, s), 6.92-7.11 (4H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.7, 30.0, 55.8, 105.3, 115.4, 117.9, 123.8, 128.0, 129.5, 145.8, 160.3. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$ (227.26): C, 68.70; H, 5.77; N, 18.49. Found: 68.66; H, 5.75; N, 18.49.

2-(4-Methoxyphenylamino)-5-methyl-1H-pyrrole-3-carbonitrile (7bc)

Colorless oil, IR (neat): 3379, 3298, 2891, 2254, 1521 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): 2.10 (3H, s), 3.72 (3H, s), 5.72 (1H, s), 5.79 (1H, br.s, *NH*), 6.79-6.87 (4H, m), 7.73 (1H, br.s, *NH*); ^{13}C NMR (100 MHz, CDCl_3): 12.6, 55.3, 101.6, 106.1, 114.9, 116.8, 119.9, 121.8, 134.8, 141.2, 155.4; Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}$ (227.26): C, 68.70; H, 5.77; N, 18.49. Found: 68.67; H, 5.76; N, 18.48

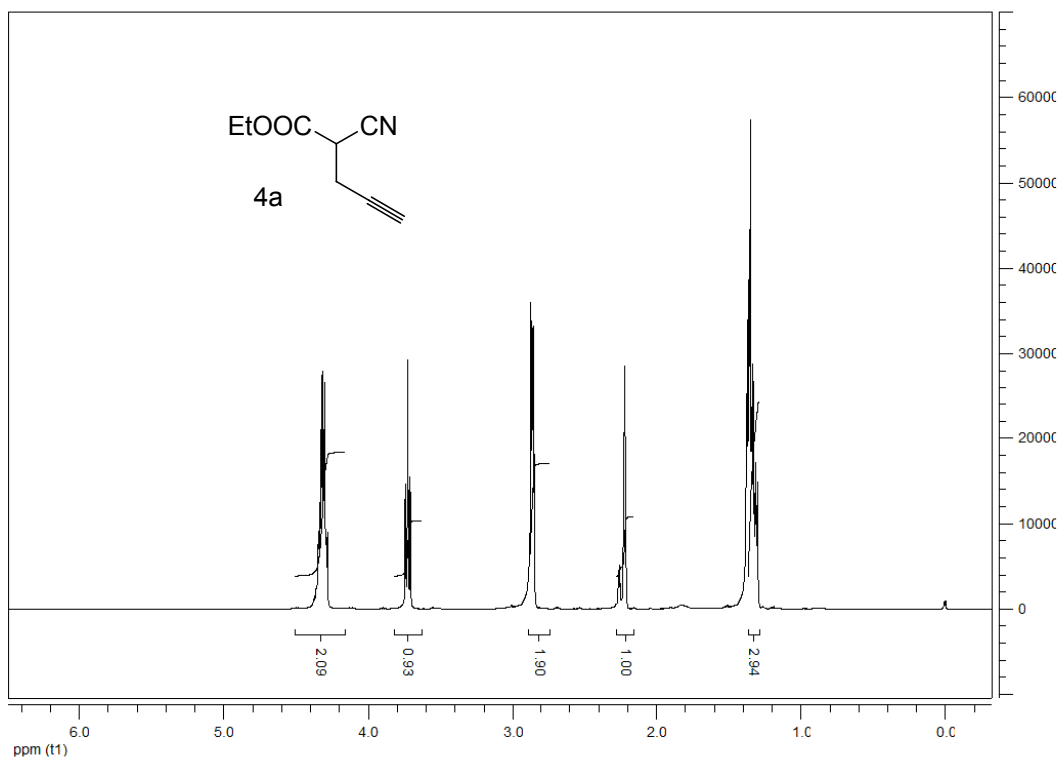
2-Amino-5-methyl-1-(4-nitrophenyl)-1H-pyrrole-3-carbonitrile (6bd)

Dark brown oil, IR (neat): 3356, 3287, 2890, 2214, 1545, 1342 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.91 (3H, s), 3.80 (2H, bs, *NH*₂), 5.91 (1H, s), 8.44 (2H, d, *J*=8.9 Hz), 8.35 (2H, d, *J*=8.9 Hz); ^{13}C NMR (100 MHz, CDCl_3): 12.6, 106.8, 116.5, 123.0, 125.2, 128.9, 134.2, 141.0, 144.5, 147.7. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$ (242.23): C, 59.50; H, 4.16; N, 23.13. Found: 59.47; H, 4.12; N, 23.15.

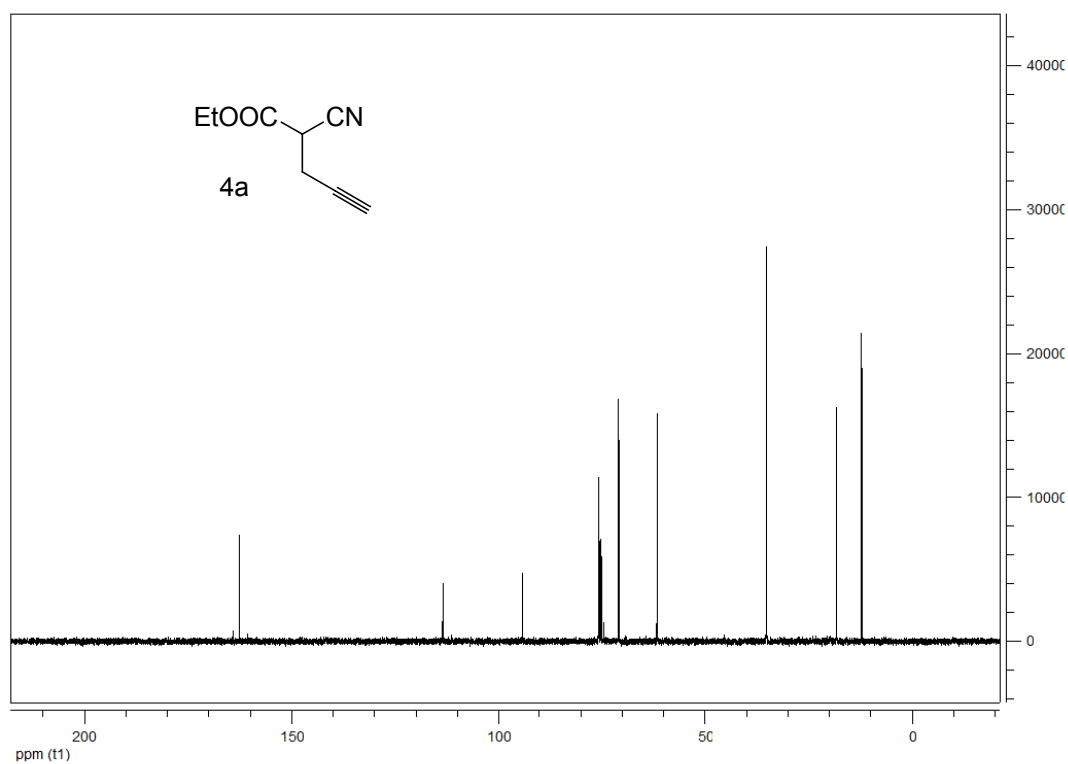
2-Amino-1-benzyl-5-methyl-1H-pyrrole-3-carbonitrile (6bg)

Colorless oil, IR (neat): 3392, 3342, 2912, 2234, 1481 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.01 (3H, s), 3.52 (2H, bs, *NH*₂), 4.91 (2H, s), 5.83 (1H, s), 6.93-7.32 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): 12.0, 46.0, 105.4, 123.5, 125.7, 127.9, 129.2, 136.0, 144.1; Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3$ (211.26): C, 73.91; H, 6.20; N, 19.89. Found: 73.87; H, 6.25; N, 19.81

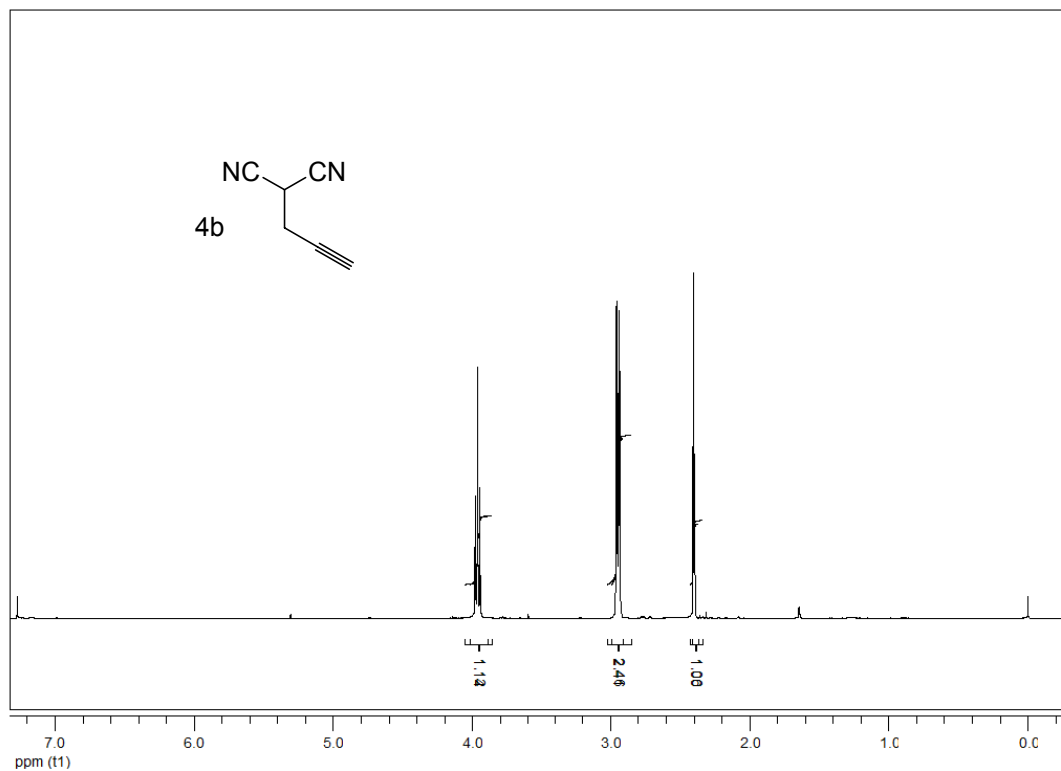
Copy of ^1H NMR and ^{13}C NMR spectra of all compounds



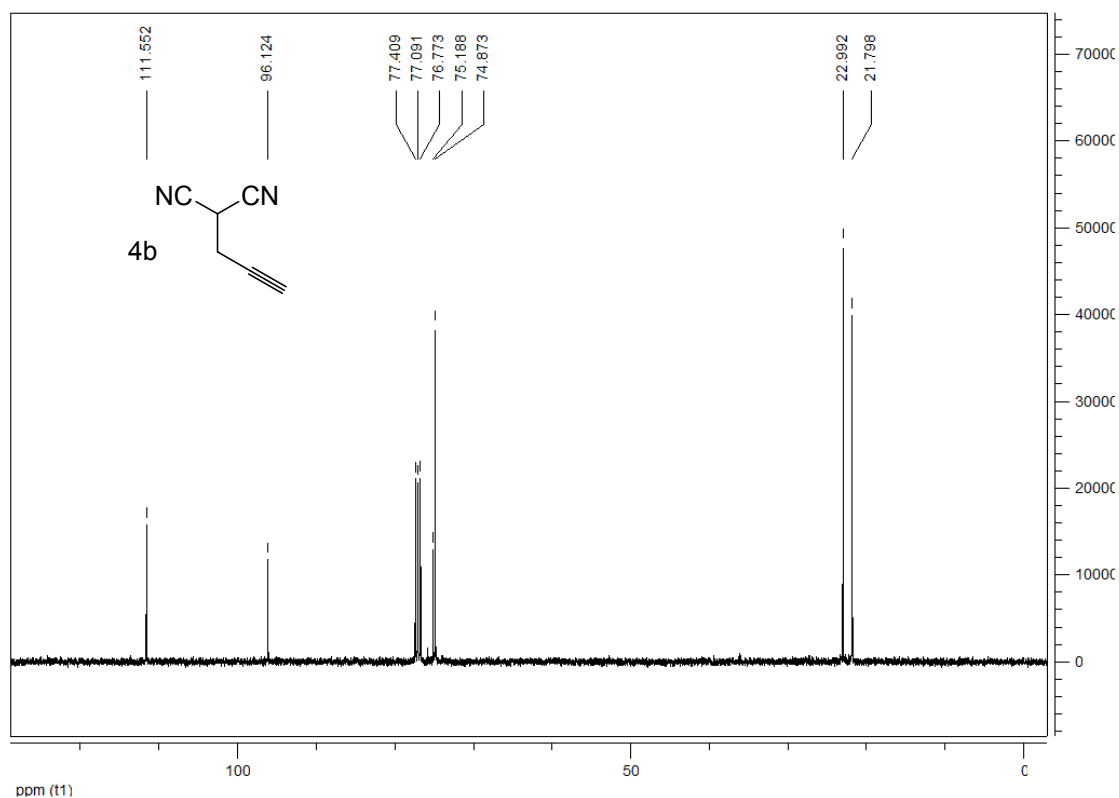
^1H NMR of ethyl 2-cyanopent-4-ynoate (4a)



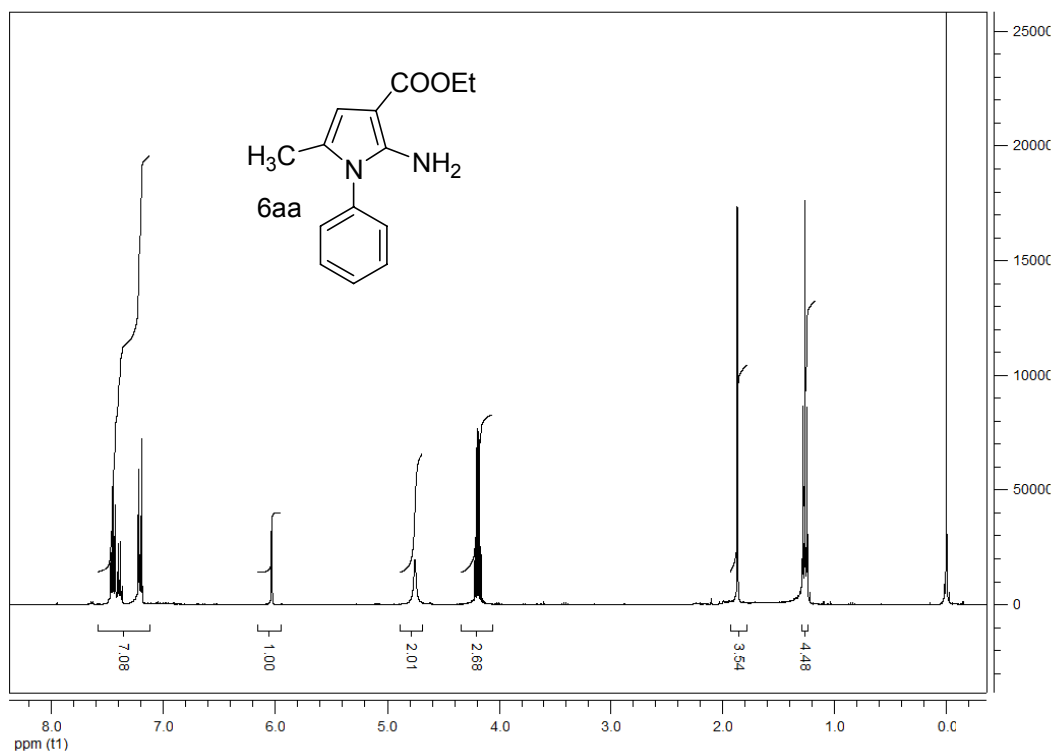
¹³C NMR of ethyl 2-cyanopent-4-ynoate (4a)



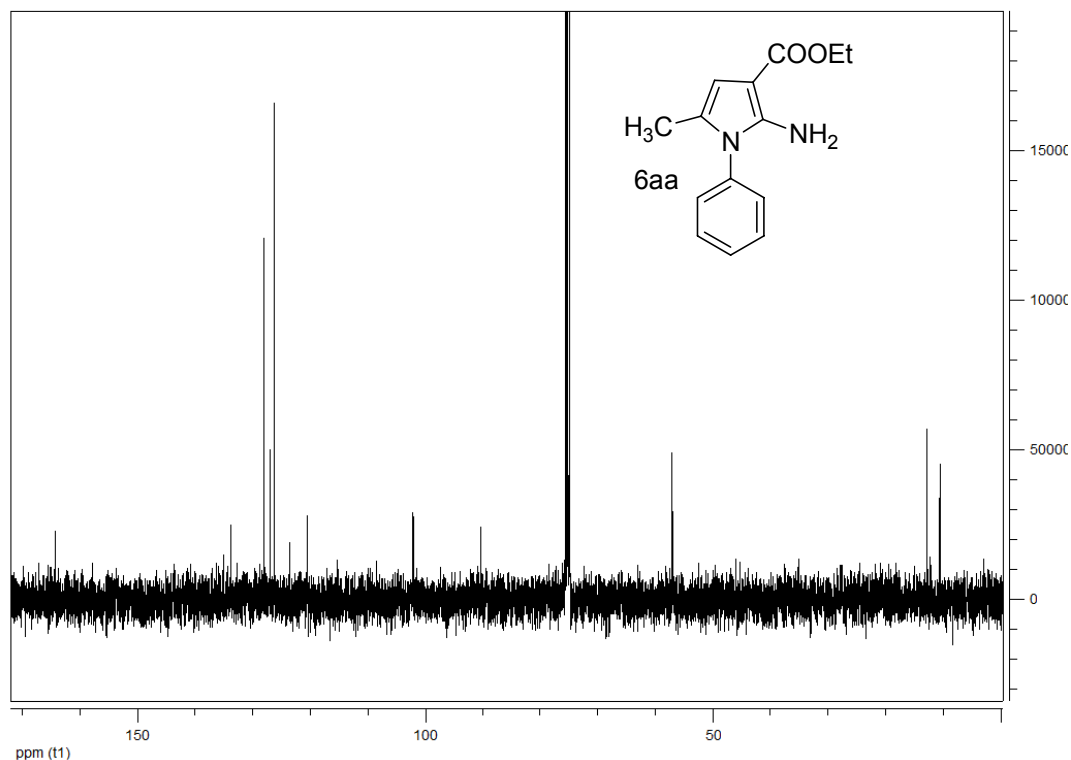
¹H NMR of 2-(prop-2-ynyl)malononitrile (4b)



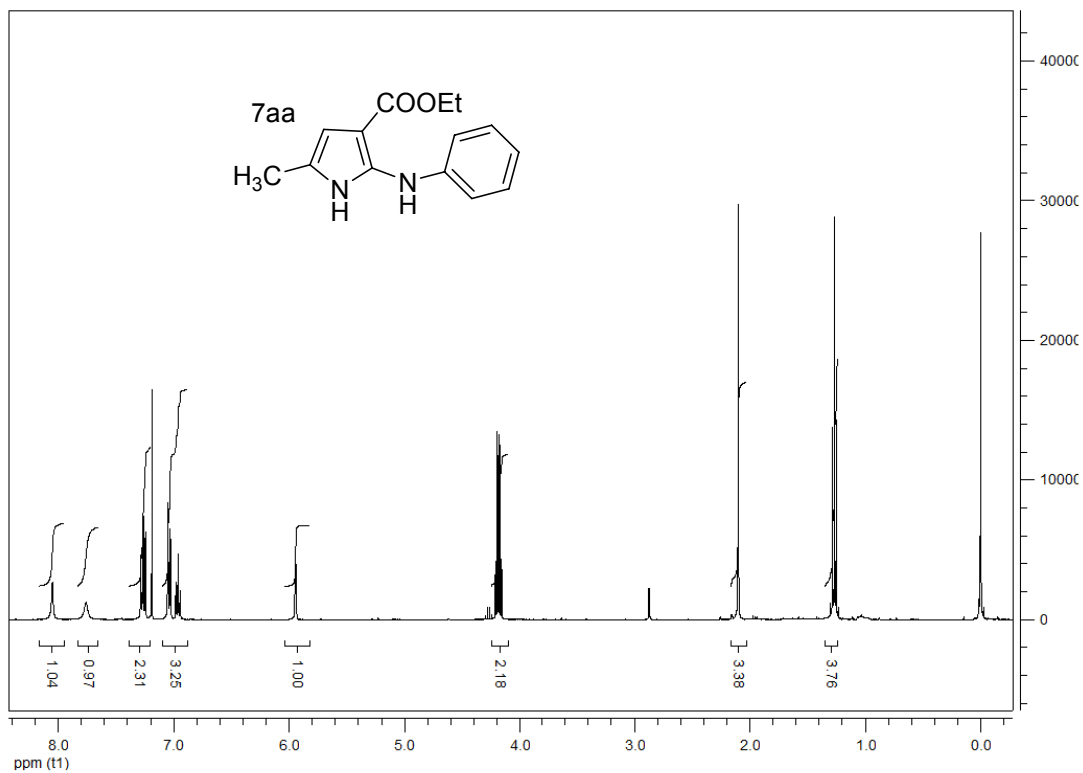
¹³C NMR of 2-(prop-2-ynyl)malononitrile (4b)



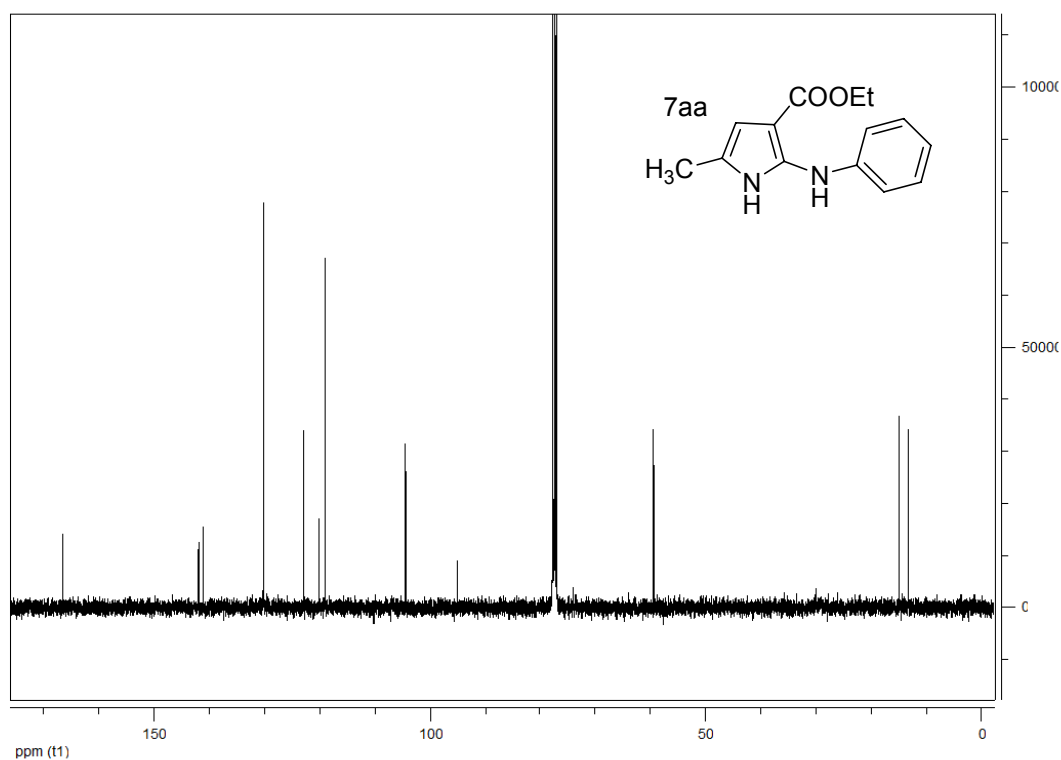
¹H NMR of Ethyl 2-amino-5-methyl-1-phenyl-1H-pyrrole-3-carboxylate (6aa)



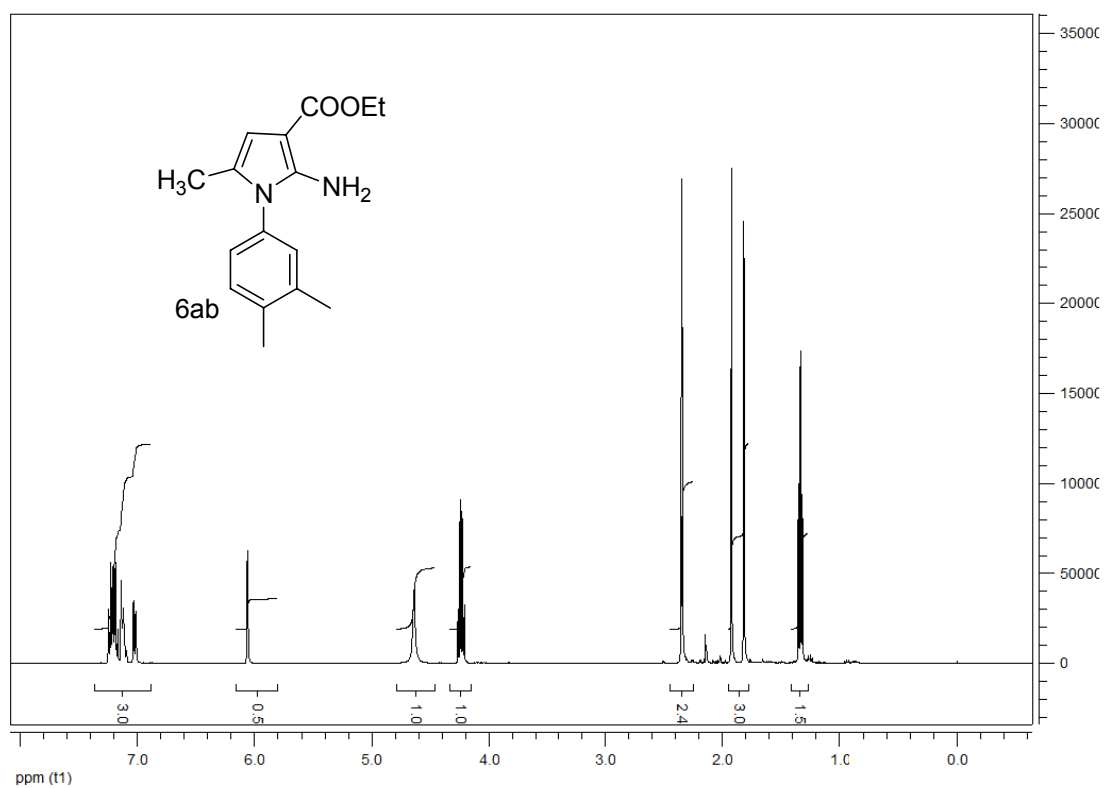
¹³C NMR of Ethyl 2-amino-5-methyl-1-phenyl-1H-pyrrole-3-carboxylate (6aa)



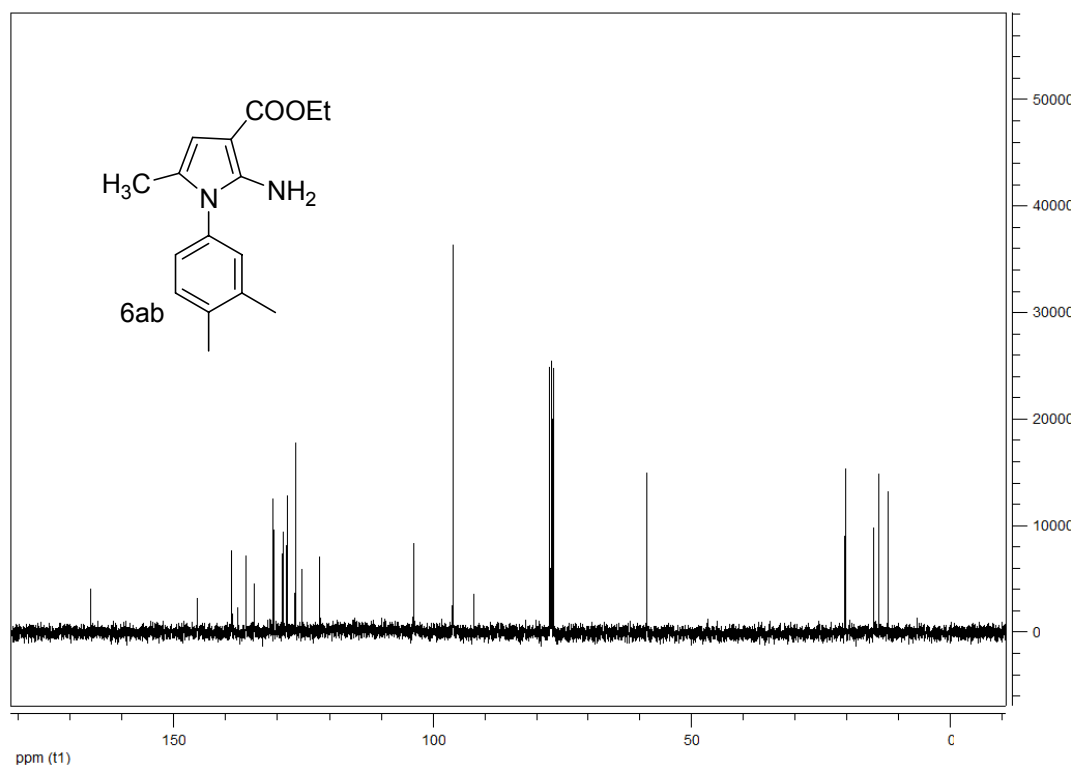
¹H NMR of ethyl 5-methyl-2-(phenylamino)-1H-pyrrole-3-carboxylate (7aa)



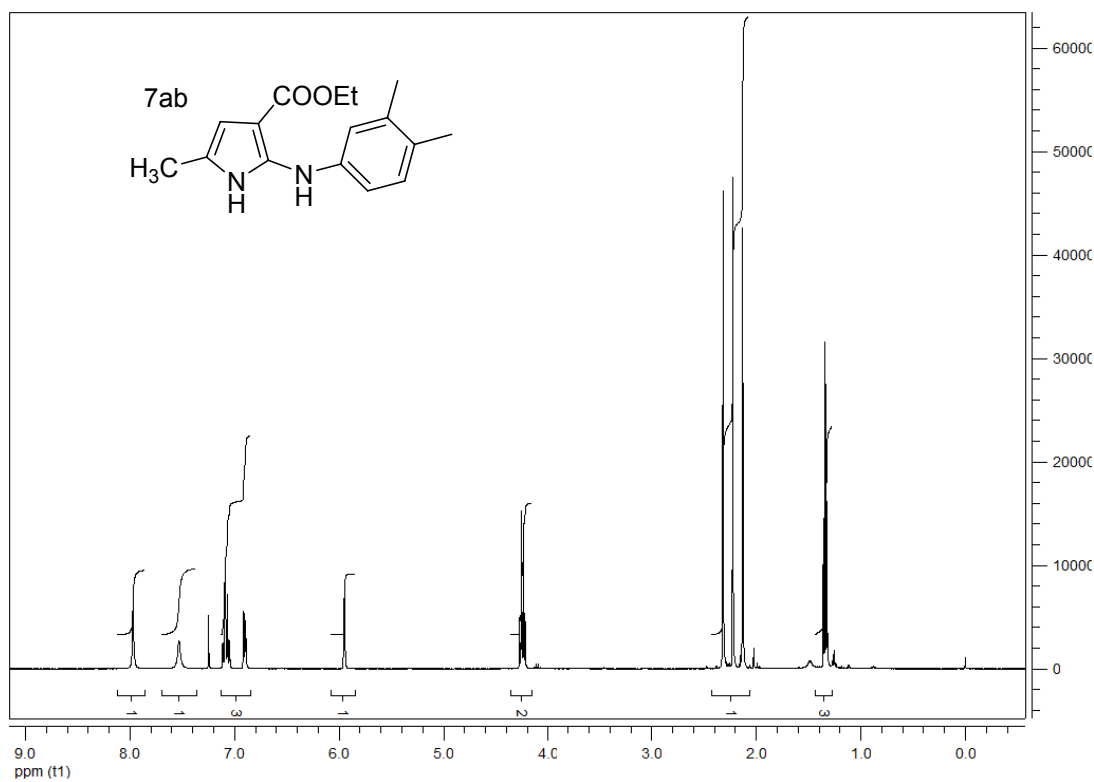
¹³C NMR of ethyl 5-methyl-2-(phenylamino)-1*H*-pyrrole-3-carboxylate (7aa)



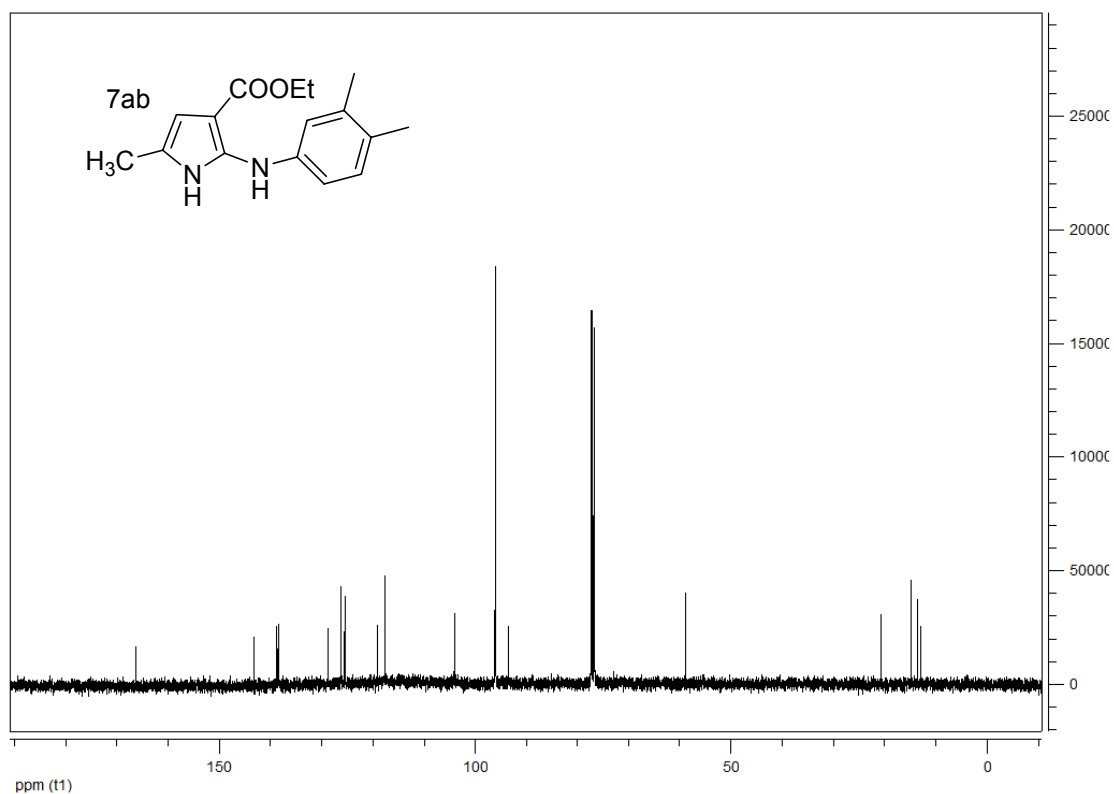
¹H NMR of ethyl 2-amino-5-methyl-1-(2,3-dimethylphenyl)-1*H*-pyrrole-3-carboxylate (6ab)



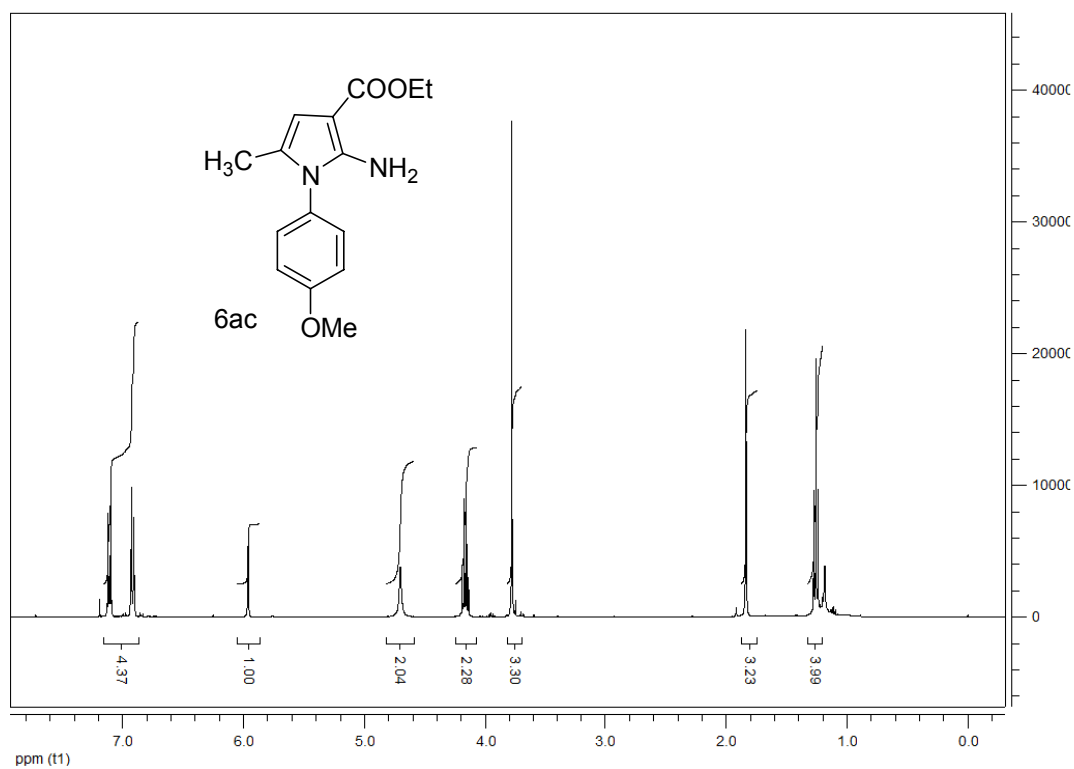
¹³C NMR of ethyl 2-amino-5-methyl-1-(2,3-dimethylphenyl)-1H-pyrrole-3-carboxylate (6ab)



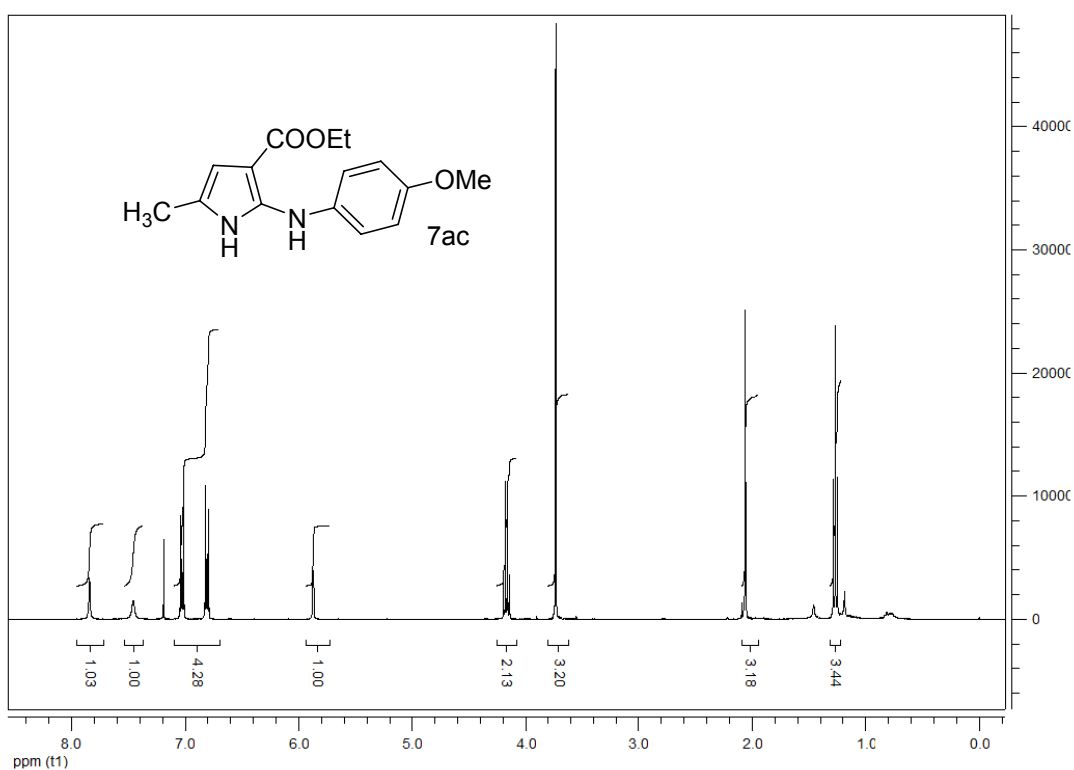
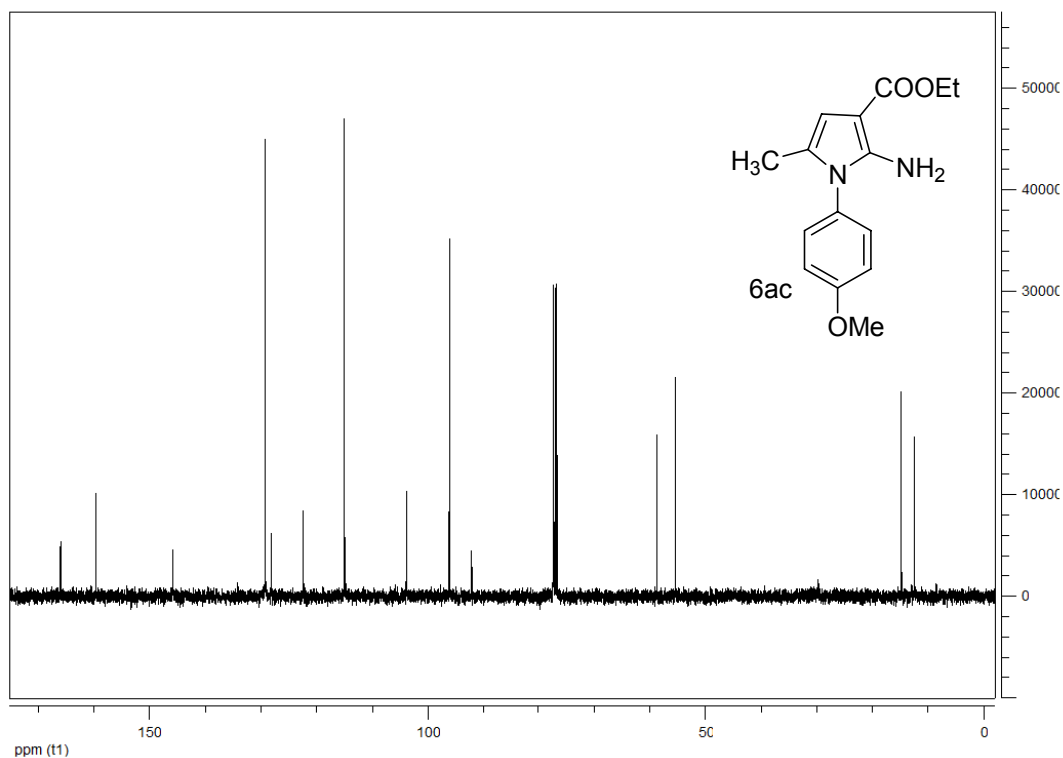
¹H NMR of ethyl 2-(2,3-dimethylphenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ab)

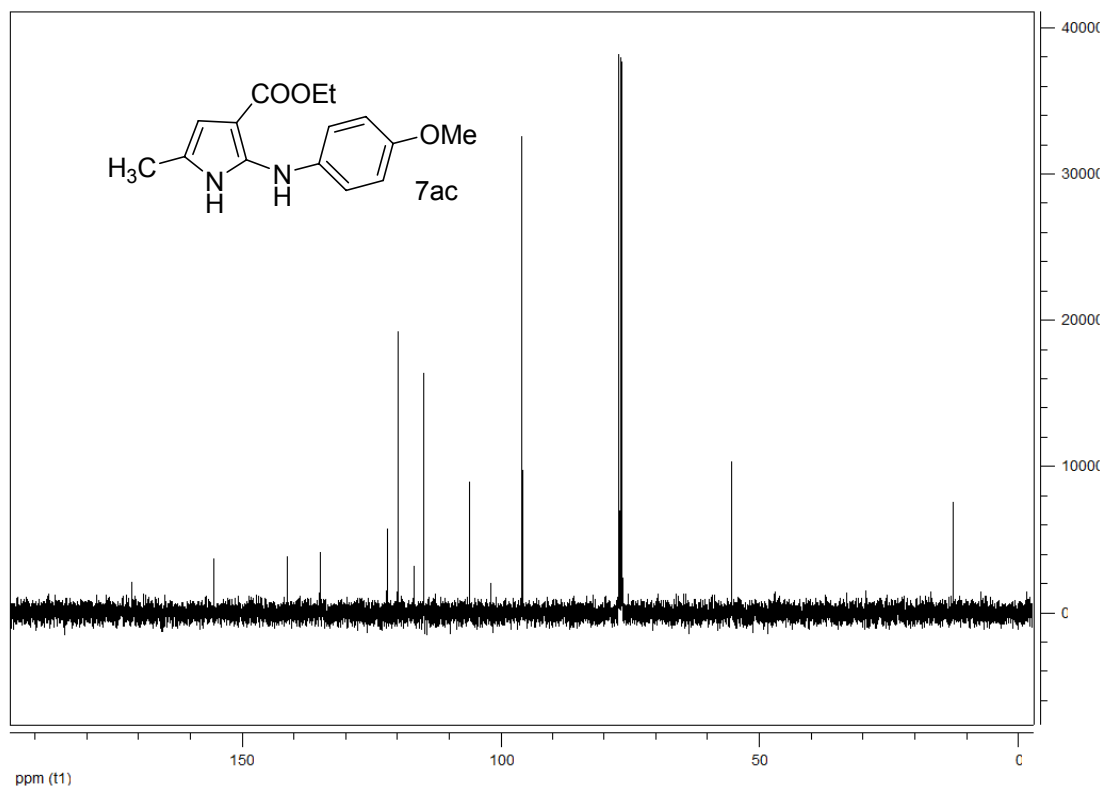


¹³C NMR of ethyl 2-(2,3-dimethylphenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ab)

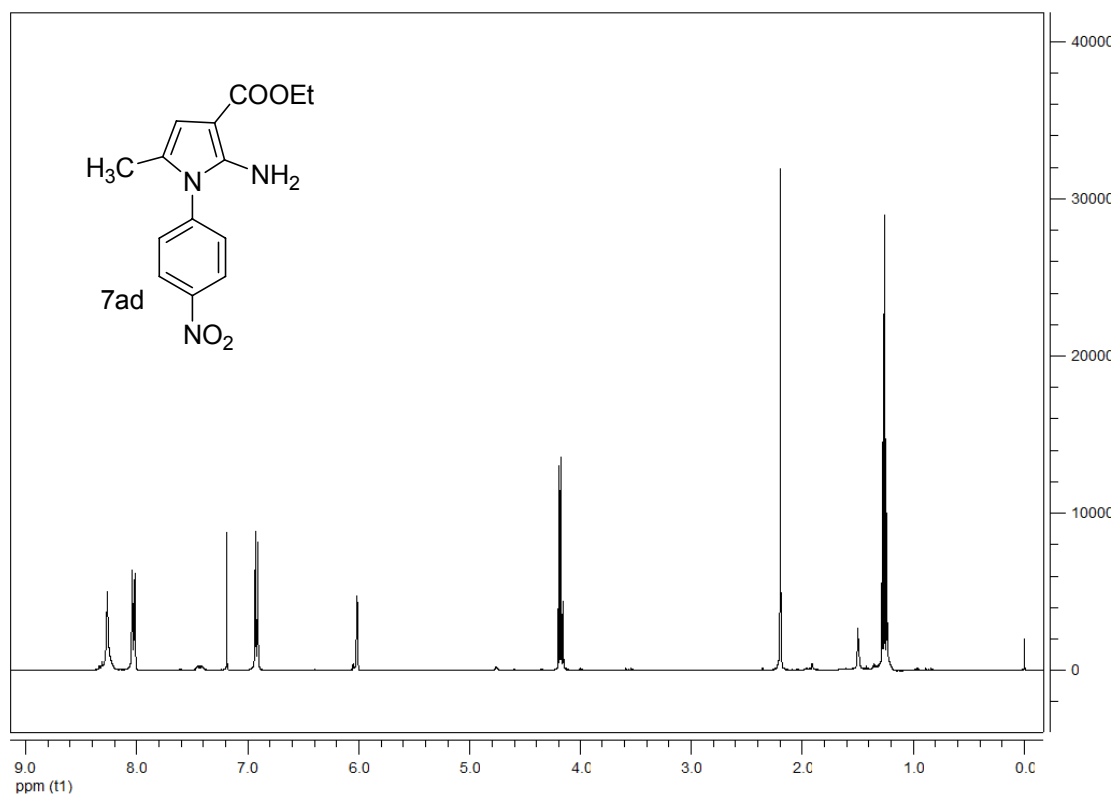


¹H NMR of ethyl 2-amino-1-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carboxylate (6ac)

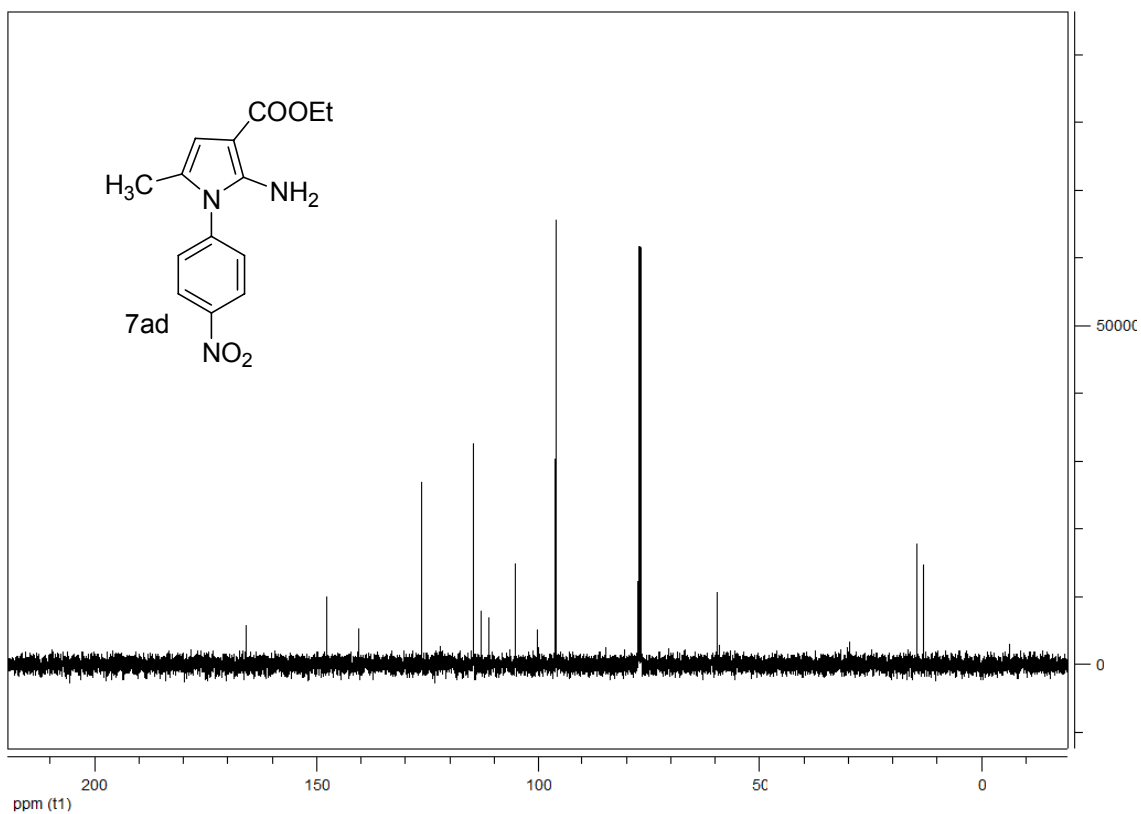




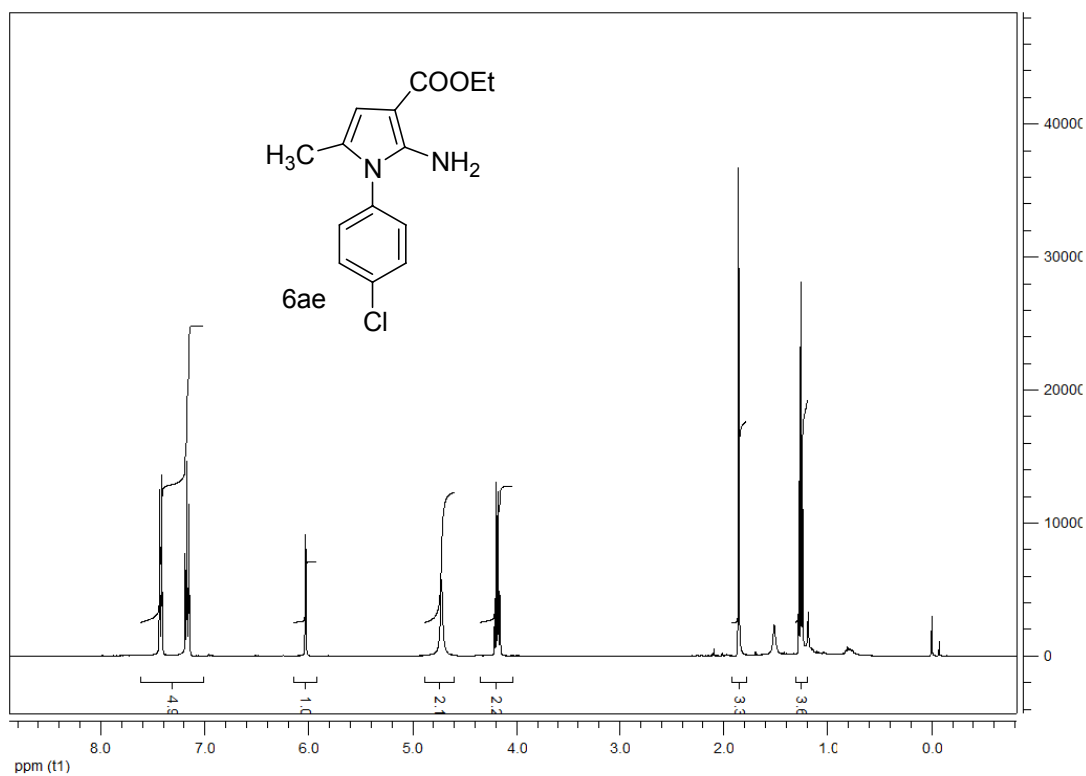
¹³C NMR of ethyl 2-(4-methoxyphenylamino)-5-methyl-1*H*-pyrrole-3-carboxylate (7ac)



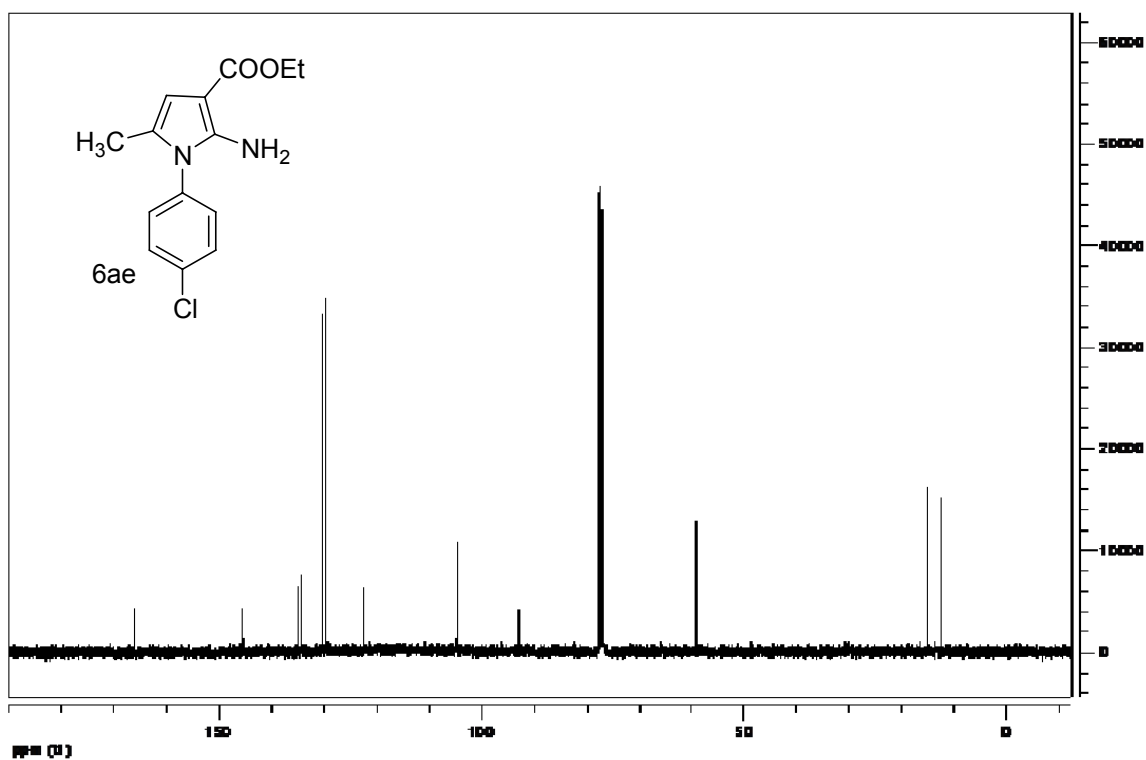
¹H NMR of ethyl 5-methyl-2-(4-nitrophenylamino)-1*H*-pyrrole-3-carboxylate (7ad)



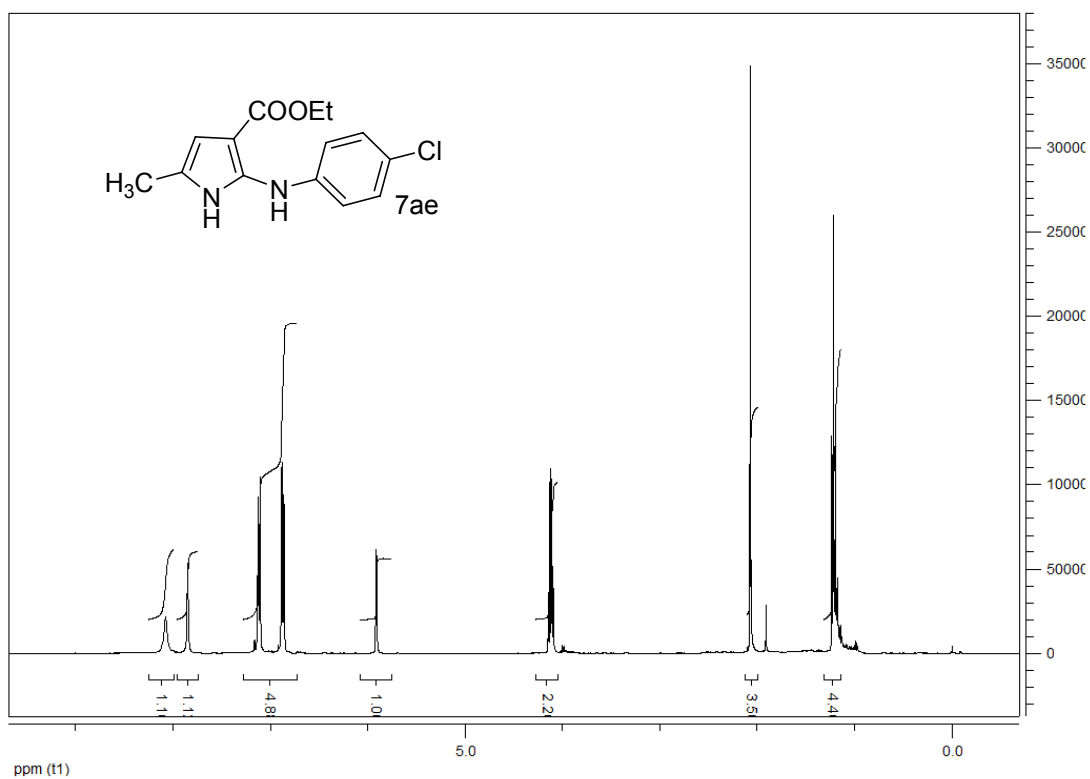
¹³C NMR of ethyl 5-methyl-2-(4-nitrophenylamino)-1H-pyrrole-3-carboxylate (7ad)



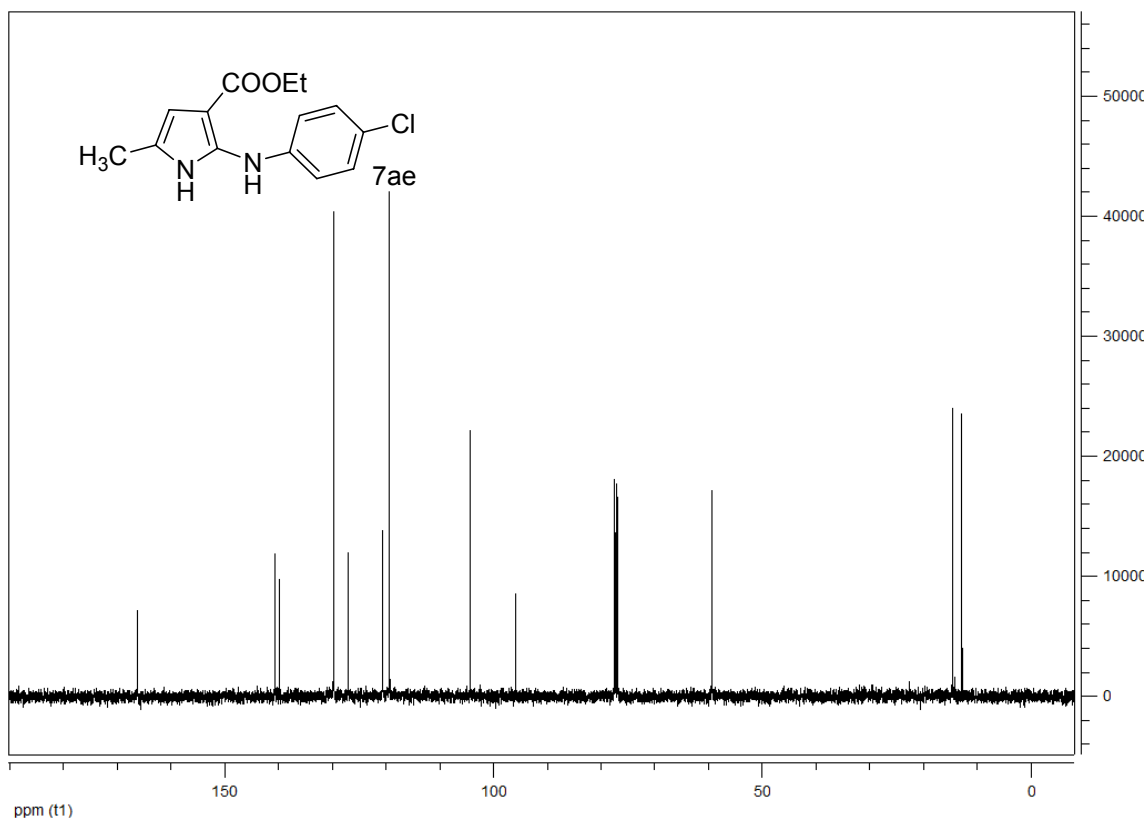
¹H NMR of ethyl 2-amino-1-(4-chlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (6ae)



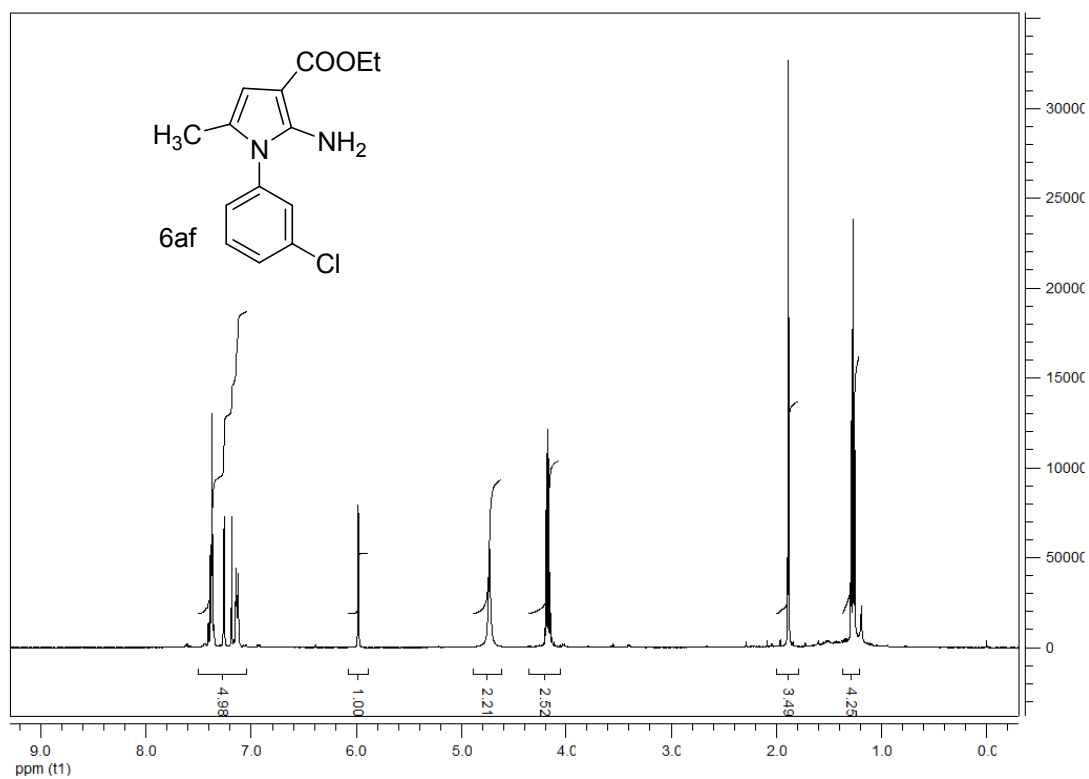
¹³C NMR of ethyl 2-amino-1-(4-chlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (6ae)



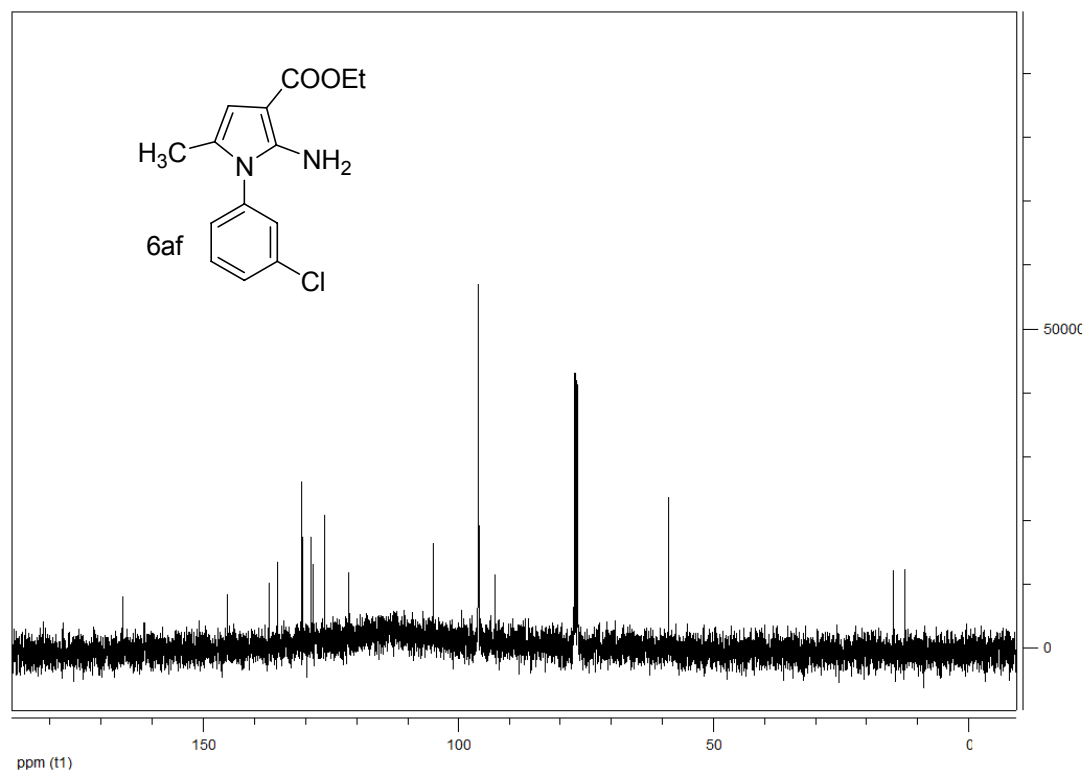
¹H NMR of ethyl 2-(4-chlorophenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ae)



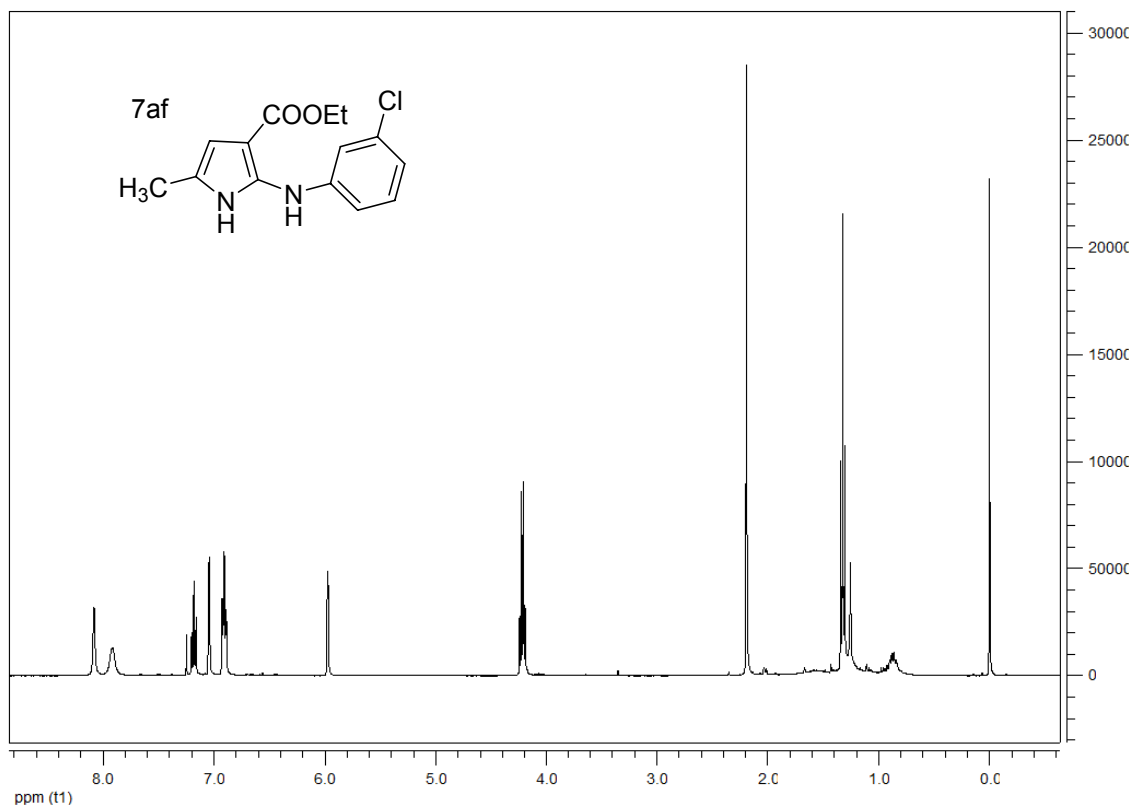
^{13}C NMR of ethyl 2-(4-chlorophenylamino)-5-methyl-1*H*-pyrrole-3-carboxylate (7ae)



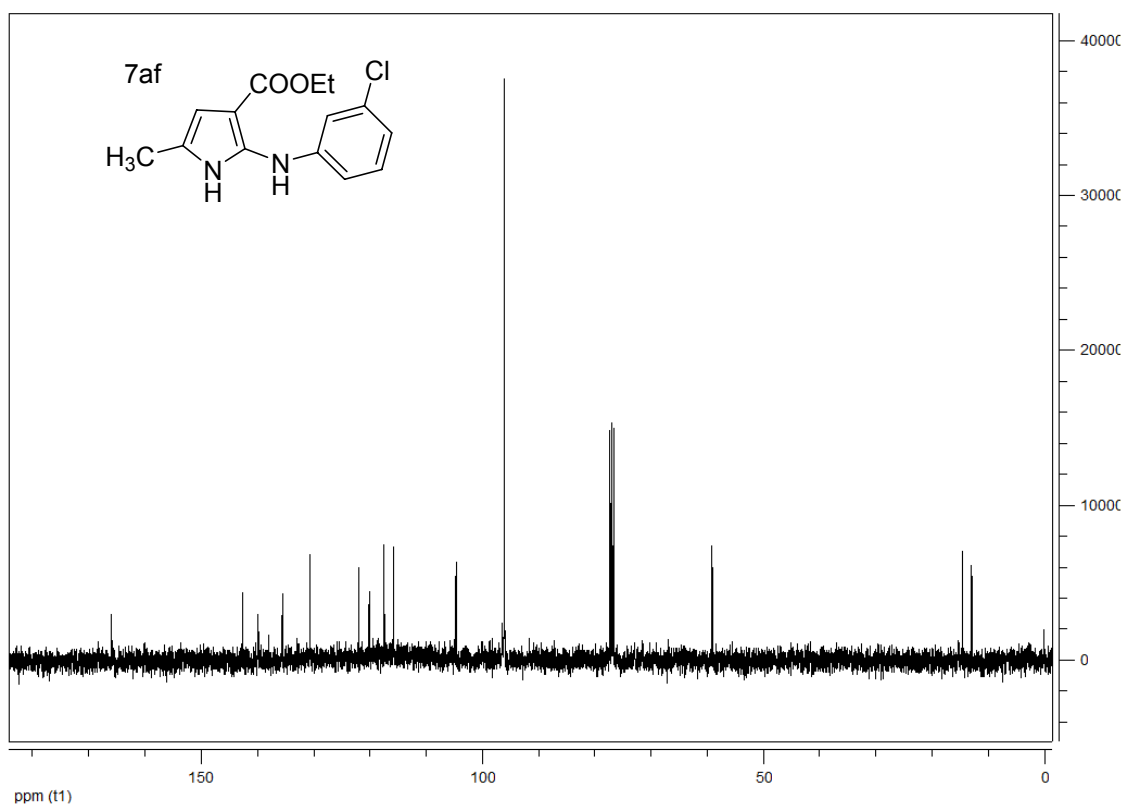
^1H NMR of Ethyl 2-amino-1-(3-chlorophenyl)-5-methyl-1*H*-pyrrole-3-carboxylate (6af)



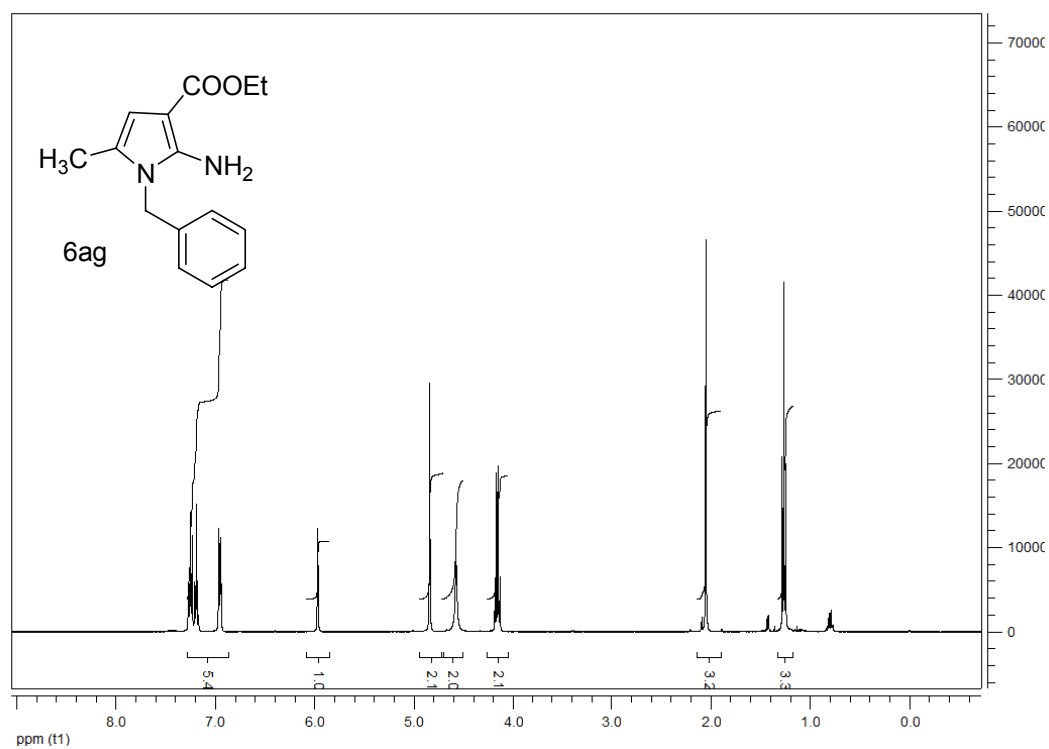
¹³C NMR of Ethyl 2-amino-1-(3-chlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (6af)



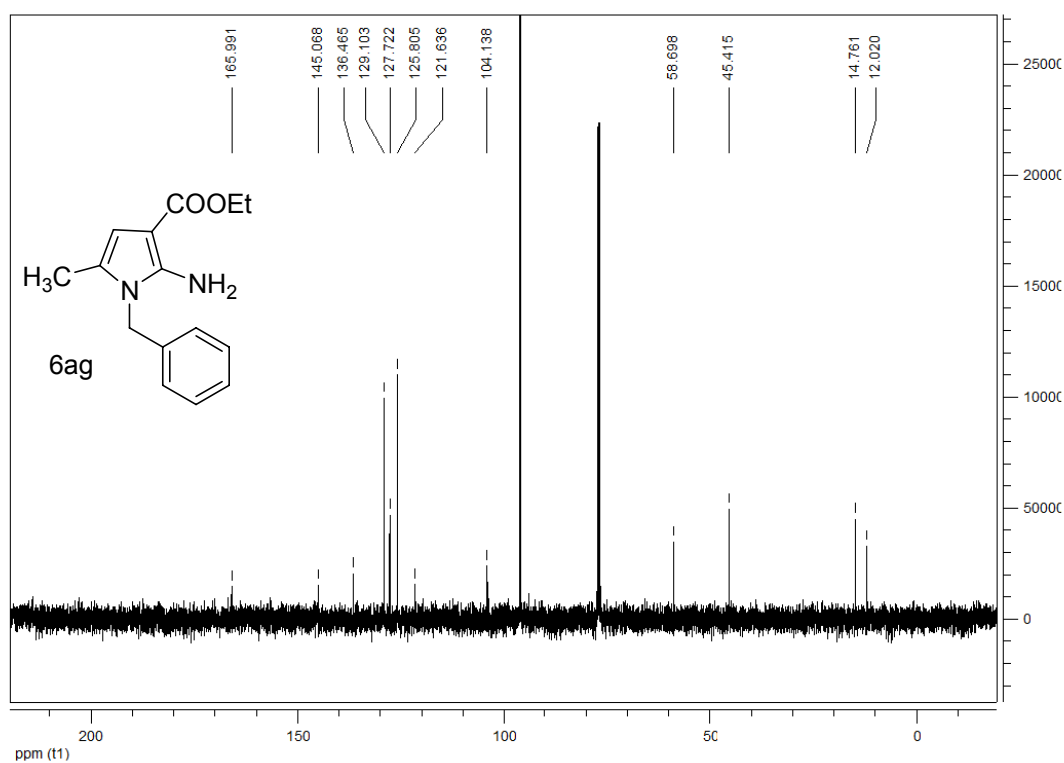
¹H NMR of ethyl 2-(3-chlorophenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7af)



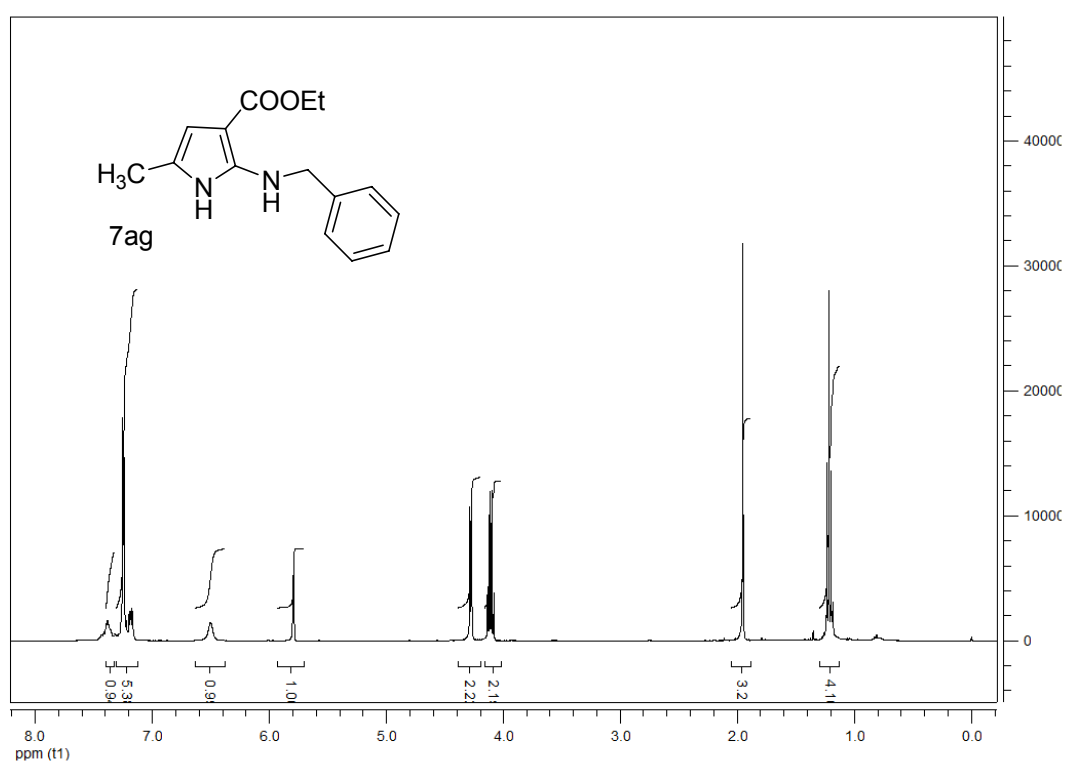
¹³C NMR of ethyl 2-(3-chlorophenylamino)-5-methyl-1H-pyrrole-3-carboxylate (7af)



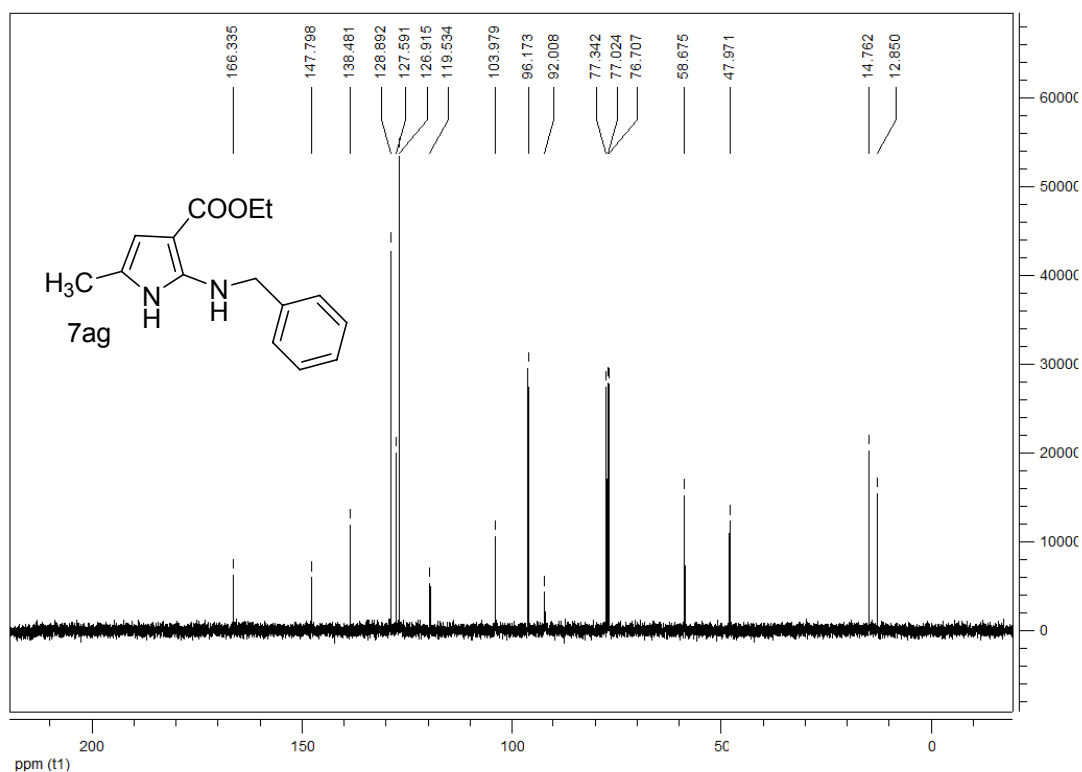
¹H NMR of ethyl 2-amino-1-benzyl-5-methyl-1H-pyrrole-3-carboxylate (6ag)



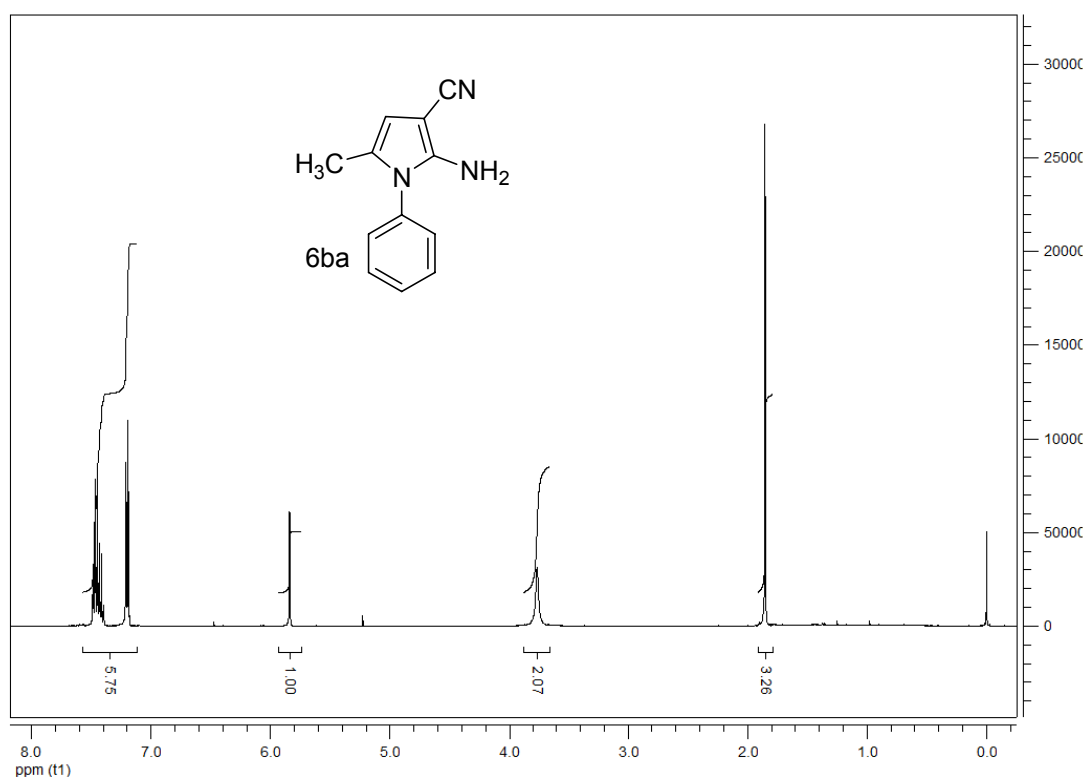
¹³C NMR of ethyl 2-amino-1-benzyl-5-methyl-1H-pyrrole-3-carboxylate (6ag)



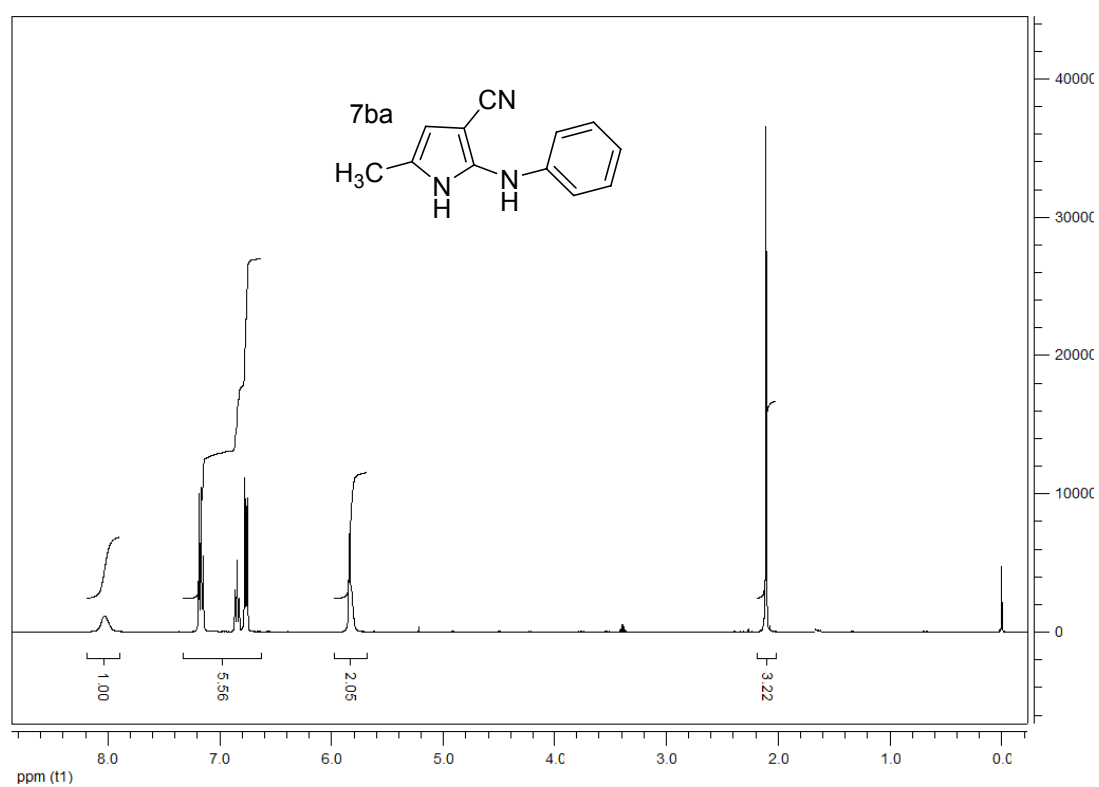
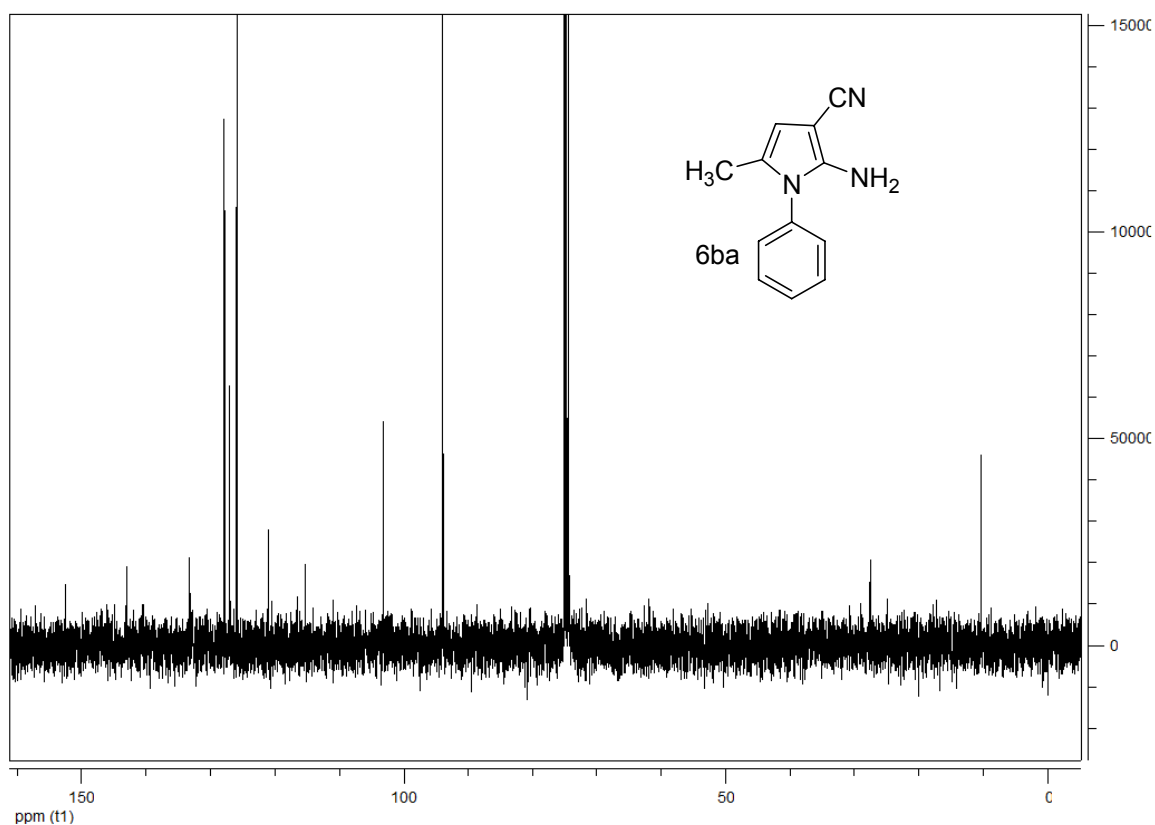
¹H NMR of ethyl 2-(benzylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ag)

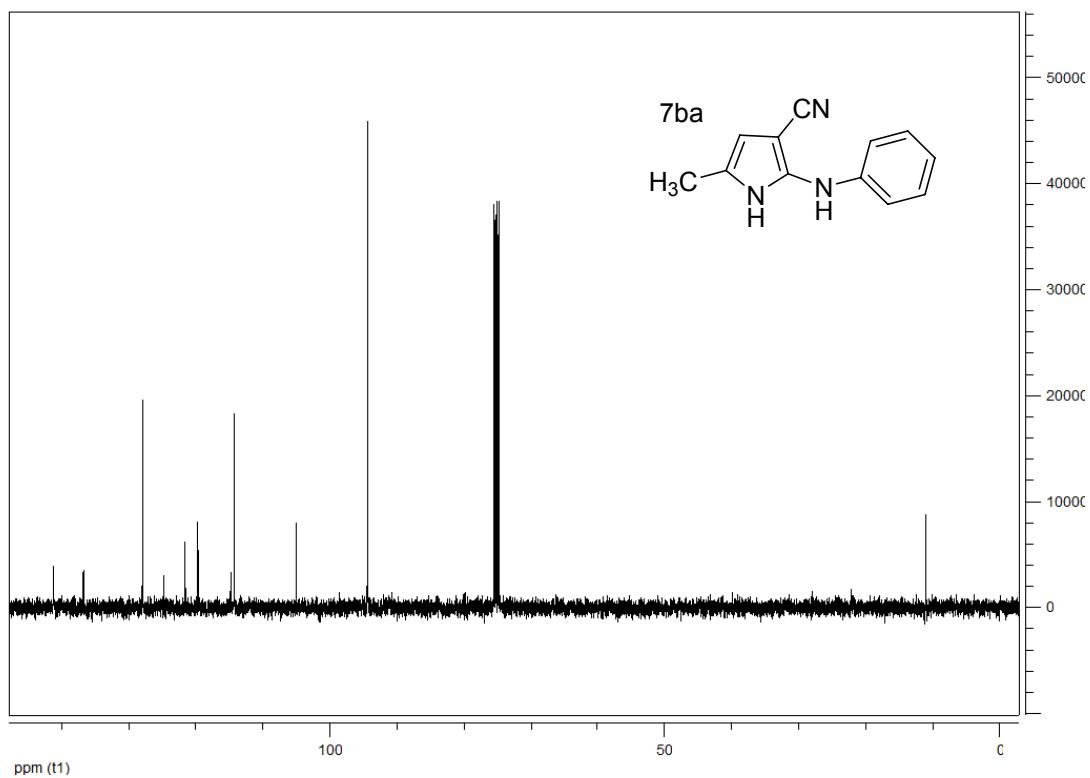


¹³C NMR of ethyl 2-(benzylamino)-5-methyl-1H-pyrrole-3-carboxylate (7ag)

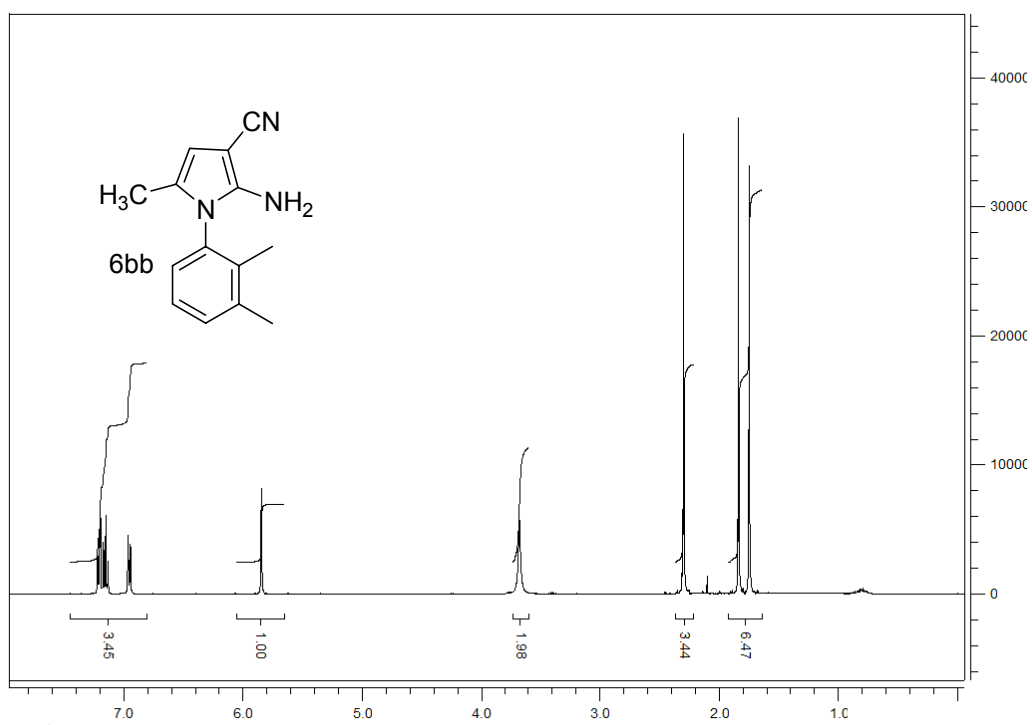


¹H NMR of 2-amino-5-methyl-1-phenyl-1H-pyrrole-3-carbonitrile (6ba)

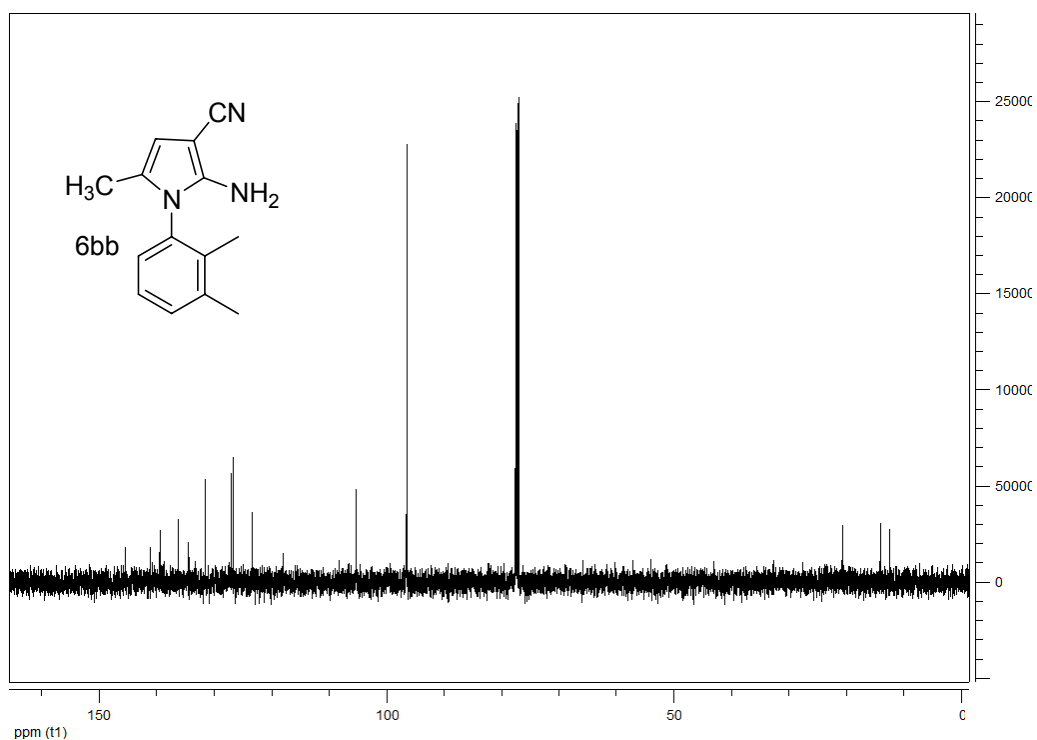




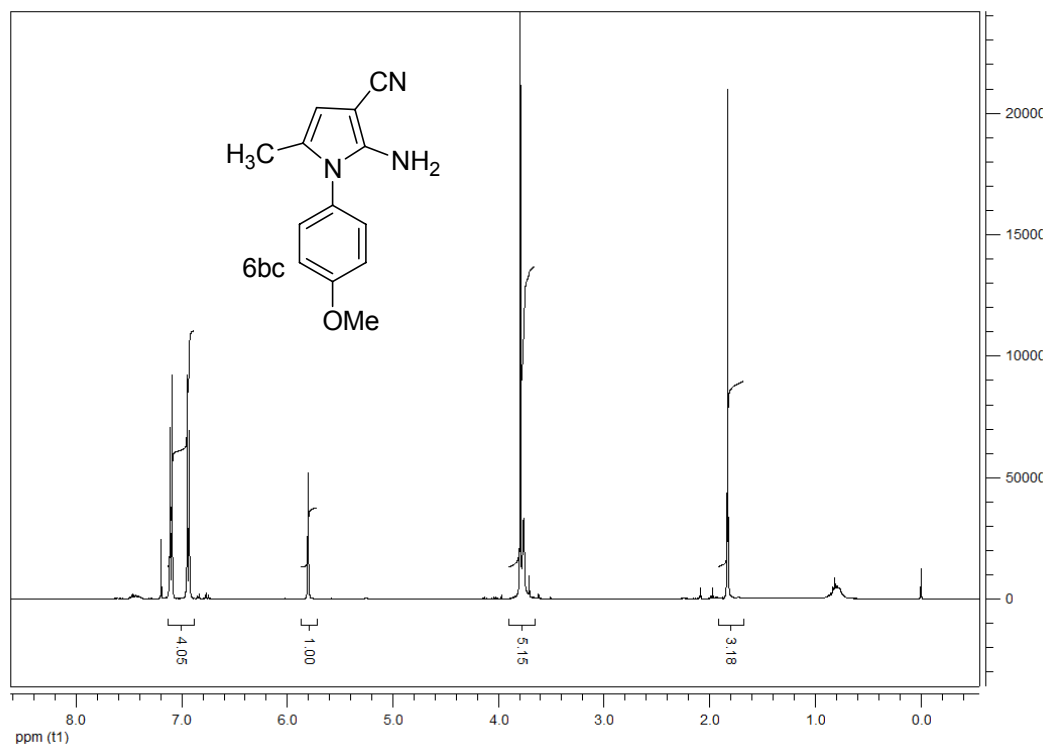
¹³C NMR of 5-methyl-2-(phenylamino)-1*H*-pyrrole-3-carbonitrile (7ba)



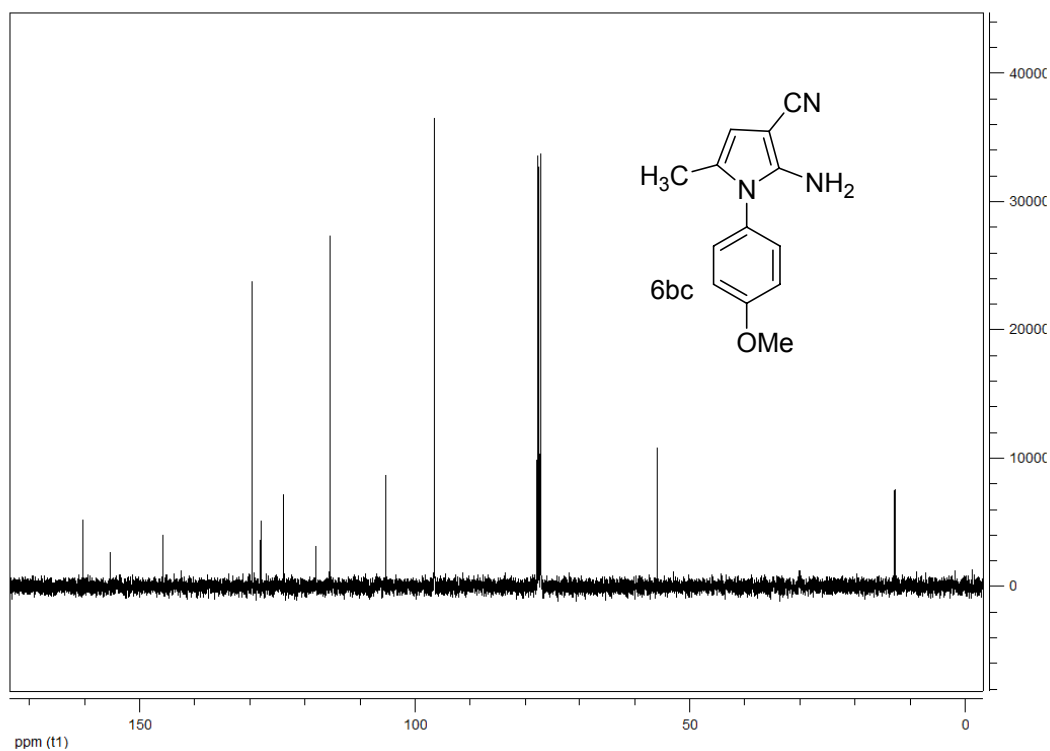
¹H NMR of 2-amino-1-(2,3-dimethylphenyl)-5-methyl-1*H*-pyrrole-3-carbonitrile (6bb)



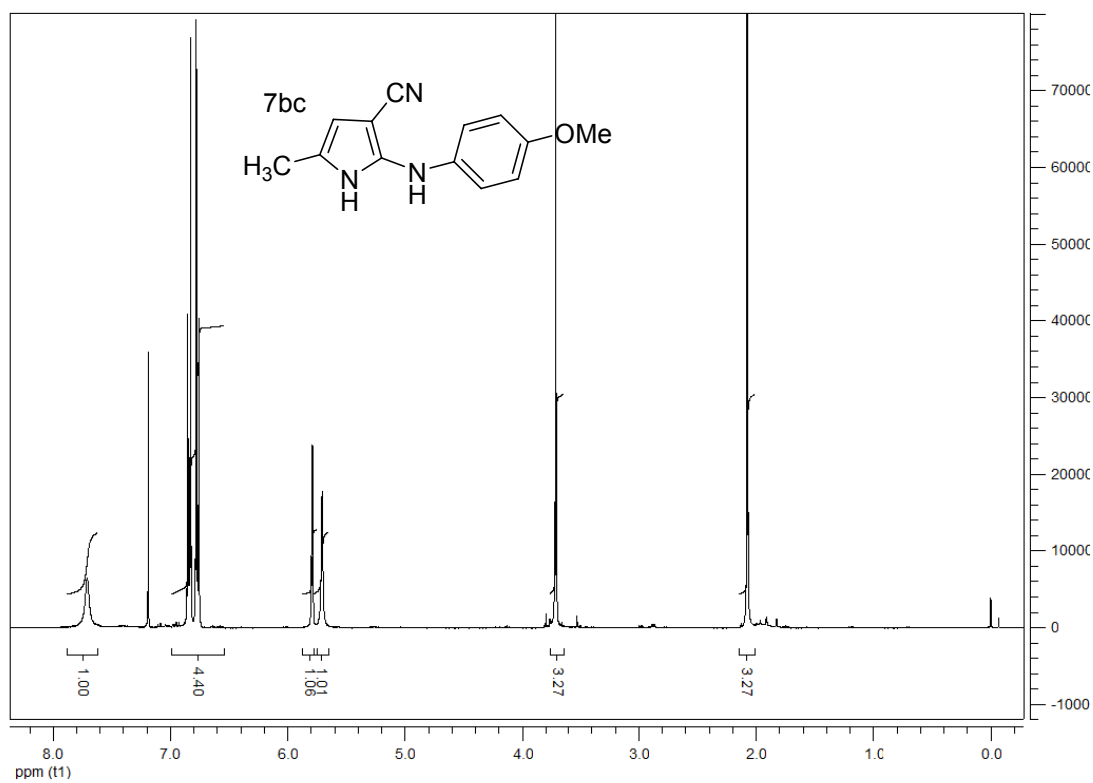
¹³C NMR of 2-amino-1-(2,3-dimethylphenyl)-5-methyl-1H-pyrrole-3-carbonitrile (6bb)



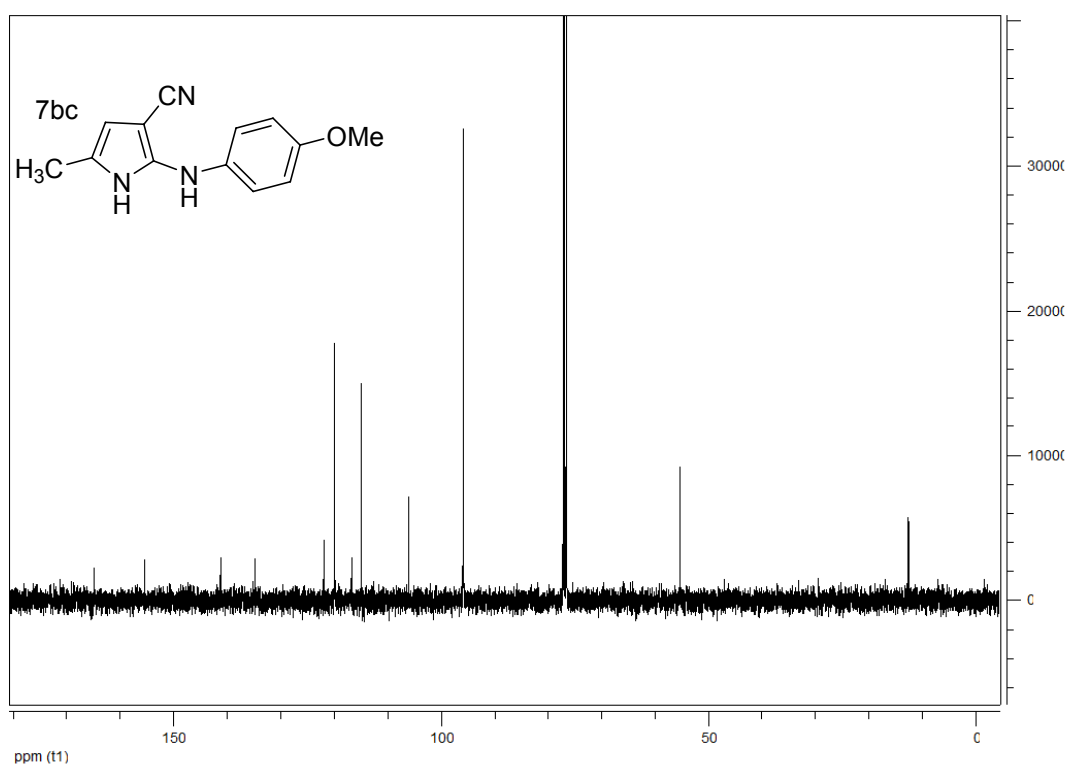
¹H NMR of 2-amino-1-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carbonitrile (6bc)



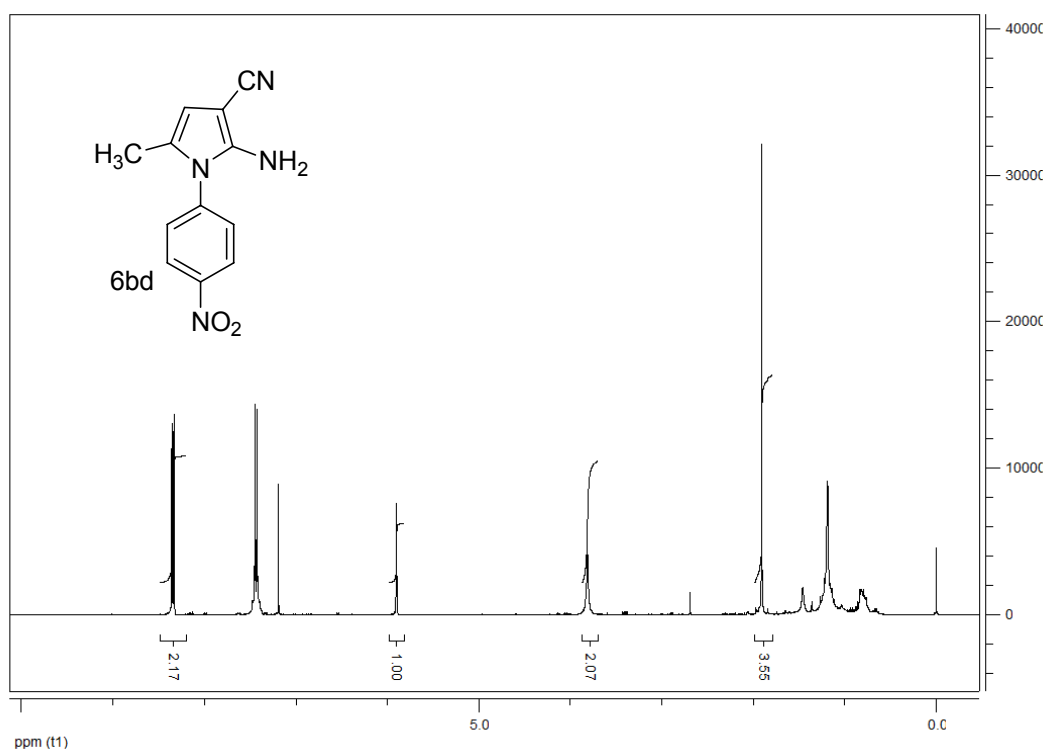
¹³C NMR of 2-amino-1-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carbonitrile (6bc)



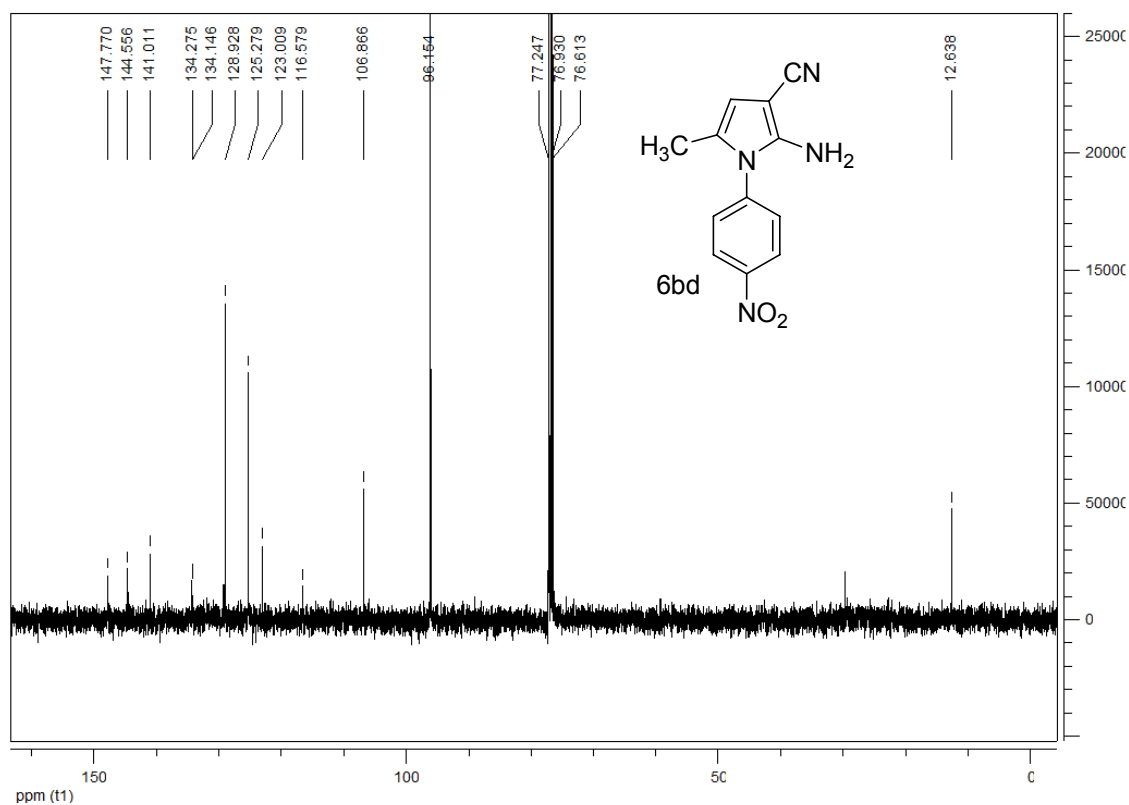
¹H NMR of 2-(4-Methoxyphenylamino)-5-methyl-1*H*-pyrrole-3-carbonitrile (7bc)



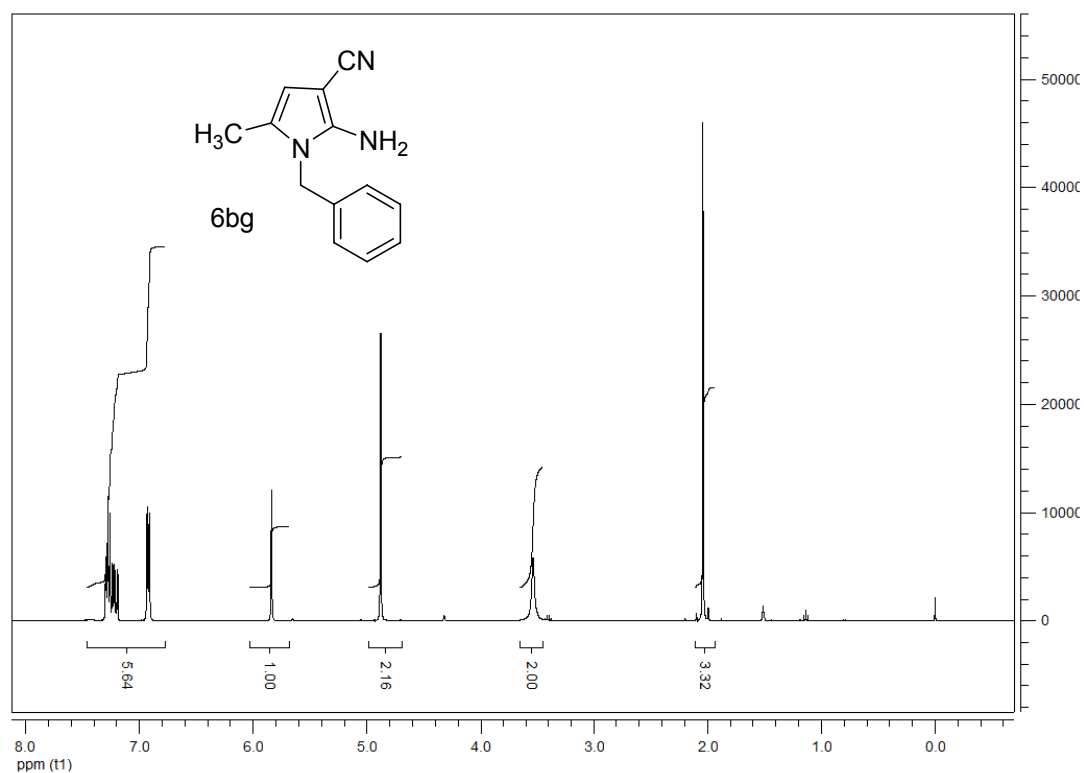
¹³C NMR of 2-(4-Methoxyphenylamino)-5-methyl-1*H*-pyrrole-3-carbonitrile (7bc)



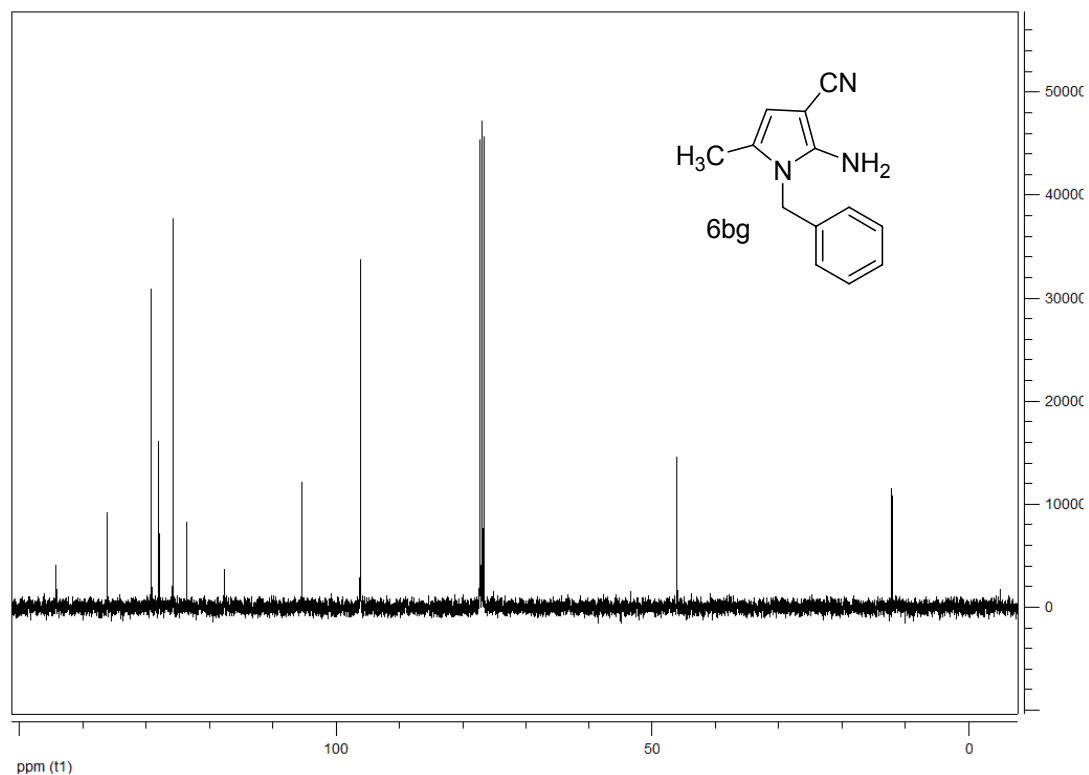
¹H NMR- of 2-amino-5-methyl-1-(4-nitrophenyl)-1*H*-pyrrole-3-carbonitrile (6bd)



¹³C NMR- of 2-amino-5-methyl-1-(4-nitrophenyl)-1*H*-pyrrole-3-carbonitrile (6bd)



¹H NMR of 2-amino-1-benzyl-5-methyl-1*H*-pyrrole-3-carbonitrile (6bg)



^{13}C NMR of 2-amino-1-benzyl-5-methyl-1*H*-pyrrole-3-carbonitrile (6bg)