

Highly Efficient Copper-Catalyzed *N*-Arylation of Nitrogen-Containing Heterocycles with Aryl and Heteroaryl Halides

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Supporting Information

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I. General Remarks

The ^1H NMR (300 MHz, 400 MHz or 600 MHz) chemical shifts were measured relative to tetramethylsilane, CDCl_3 or CD_3OD as the internal reference. The ^{13}C NMR (50 MHz, 75 MHz, 100 MHz or 150 MHz) chemical shifts are given using CDCl_3 or CD_3OD as the internal standard. Low-resolution mass spectra (MS) were obtained by EI or ESI or GC-MS (EI) and high resolution mass spectra (HRMS) were recorded by FAB with *m*-NBA or EI.

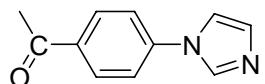
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing for at least 24 h over CaH_2 (chloroform, DMF or DMSO), sodium/benzophenone (THF or toluene), and freshly distilled prior to use. CuI should be washed with THF using a Soxhlet extractor before it is used to ensure satisfactory catalytic activity. Unless otherwise indicated, all syntheses and manipulations were carried out under dry dinitrogen atmosphere.

II. General procedure for the catalytic *N*-arylation of nitrogen-containing heterocycles with aryl halides

To a flame-dried Schlenk test tube with a magnetic stirring bar was charged with CuI (9.6 mg, 0.05 mmol), ligand (0.1 mmol), Cs_2CO_3 (0.652 g, 2.0 mmol), nitrogen-containing heterocycle (1.0 mmol), aryl or heteroaryl halide (1.2 mmol) and DMF (2 mL) under N_2 . A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2 . The reaction mixture was stirred for 30 min at room temperature, and then heated to 110 °C for 24 h. The reaction mixture was then cooled to

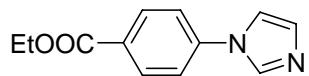
ambient temperature, diluted with 2-3 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

III. Synthesis and analytical data of 7a-7z



1-(4-Imidazol-1-yl-phenyl)-ethanone (7b)¹

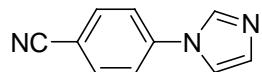
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 4-bromoacetophenone (0.239 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (99% yield). ¹H NMR (600 MHz, CDCl₃): δ 2.65 (s, 3H), 7.33 (bs, 1H), 7.45 (bs, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 8.05 (bs, 1H), 8.09 (d, *J* = 8.4 Hz, 2H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 26.6, 117.7, 120.7, 130.3, 131.1, 135.4, 135.7, 140.7, 196.5 ppm. GC-MS (EI, *m/z*): 186 [M⁺].



4-Imidazol-1-yl-benzoic acid ethyl ester (7c)¹

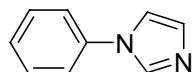
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with ethyl 4-bromobenzoate (196 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white

solid (61% yield). ^1H NMR (400 MHz, CDCl_3): δ 1.36 (t, $J = 7.6$ Hz, 3H), 4.36 (m, 2H), 7.25 (bs, 1H), 7.36 (bs, 1H), 7.45-7.47 (m, 2H), 7.96 (bs, 1H), 8.11-8.16 (m, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 61.3, 117.9, 120.1, 120.5, 129.4, 131.1, 131.5, 140.6, 165.5 ppm. GC-MS (EI, m/z): 216 [M^+]



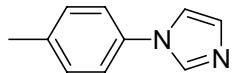
4-Imidazol-1-yl-benzonitrile (7d)²

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 4-bromobenzonitrile (0.216 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (95% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.27 (s, 1H), 7.35 (s, 1H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.99 (s, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 110.9, 117.5, 117.8, 121.3, 131.4, 134.1, 135.2, 140.4 ppm. GC-MS (EI, m/z): 169 [M^+].



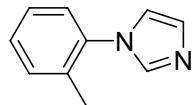
1-Phenyl-1H-imidazole (7a)²

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with bromobenzene (126 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (96% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.25 (s, 1 H), 7.32 (s, 1H), 7.38-7.41 (m, 3H), 7.49-7.51 (m, 2H), 7.92 (s, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 118.3, 121.5, 127.5, 129.9, 130.3, 135.7, 137.3 ppm. GC-MS (EI, m/z): 144 [M^+].



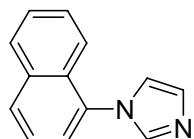
1-(4-Tolyl)-1H-imidazole (7e)²

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 4-bromotoluene (0.205 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (89% yield). ¹H NMR (600 MHz, CDCl₃): δ 2.40 (s, 3H), 7.19 (s, 1H), 7.25 (s, 1H), 7.27 (bs, 4H), 7.82 (s, 1H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 20.9, 118.3, 121.3, 130.1, 130.3, 134.9, 135.5, 137.4 ppm. GC-MS (EI, *m/z*): 158 [M⁺].



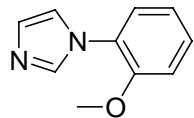
1-(2-Tolyl)-1H-imidazole (7f)¹

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromotoluene (0.205 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (78% yield). ¹H NMR (400 MHz, CDCl₃): δ 2.12 (s, 3H), 6.99 (t, *J* = 1.2 Hz, 1H) 7.13 7.31 (m, 5H) , 7.51 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 17.4, 120.3, 126.3, 126.6, 128.6, 129.1, 131.1, 133.6, 136.4, 137.3 ppm. GC-MS (EI, *m/z*): 158 [M⁺]



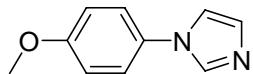
1-Naphthalen-1-yl-1H-imidazole (7g)¹

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 1-bromonaphthalene (167 μ L, 1.2 mmol) for 24 h at 110 °C in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (66% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.26 (bs, 1H), 7.31 (bs, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.52-7.62 (m, 4H), 7.78 (s, 1H), 7.95-7.97 (m, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 121.5, 122.1, 123.5, 125.0, 126.8, 127.4, 128.1, 129.1, 129.3, 129.4, 133.9, 134.0, 138.2 ppm. GC-MS (EI, *m/z*): 194 [M⁺].



1-(2-Methoxyphenyl)-1H-imidazole (7h)³

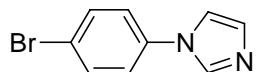
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromoanisole (149 μ L, 1.2 mmol) for 48 h at 110 °C in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (64% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.84 (s, 3H), 6.90 (bs, 1H), 7.02-7.07 (m, 2H), 7.20 (bs, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.91 (bs, 1H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ 55.6, 112.2, 120.2, 120.8, 125.3, 126.3, 128.4, 128.8, 137.6, 152.4 ppm. GC-MS (EI, *m/z*): 174 [M⁺].



1-(4-Methoxyphenyl)-1H-imidazole (7i)²

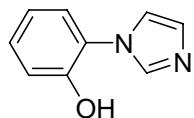
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with

4-bromoanisole (150 μ L, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (88% yield). 1 H NMR (600 MHz, CDCl₃): δ 3.86 (s, 3H), 6.99 (d, J = 8.4 Hz, 2H), 7.20 (bs, 1H), 7.22 (bs, 1H), 7.30 (d, J = 9.0 Hz, 2H), 7.79 (bs, 1H) ppm. 13 C NMR (150 MHz, CDCl₃): δ 55.6, 114.8, 118.7, 123.18, 130.0, 130.7, 135.8, 158.9 ppm. GC-MS (EI, m/z): 174 [M $^+$].



1-(4-Bromo-phenyl)-1H-imidazole (7j)¹

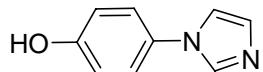
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 1,4-dibromobenzene (0.283 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (87% yield). 1 H NMR (600 MHz, CDCl₃): δ 7.23-7.30 (m, 4H), 7.61 (m, 2H), 7.85 (bs, 1H) ppm. 13 C NMR (150 MHz, CDCl₃): δ 118.0, 120.8, 122.9, 130.7, 132.9, 135.4, 136.3 ppm. GC-MS (EI, m/z): 222 [M $^+$].



2-Imidazol-1-yl-phenol (7k)³

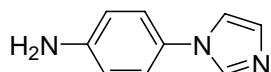
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromophenol (127 μ L, 1.2 mmol) in the presence of ligand **4a** for 48 h. The crude reaction mixture was dissolved in 20 mL of 2 M HCl, and washed once with diethyl ether. The aqueous layer was brought to pH = 7.5 with NaHCO₃, and extracted repeatedly with

CH_2Cl_2 . The combined organic layer was dried with anhydrous MgSO_4 , and concentrated under reduced pressure. The crude product was purified over a silica gel column using ethanol/ethyl acetate (1/100) to give a white solid (61% yield). ^1H NMR (400 MHz, CD_3OD): δ 6.92 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.52 (s, 1H), 8.34 (bs, 1H) ppm. ^{13}C NMR (150 MHz, CD_3OD and CDCl_3): δ 116.7, 119.3, 124.7, 128.1, 149.9 ppm. MS (ESI $^+$) m/z 161 $[\text{M}+1]^+$.



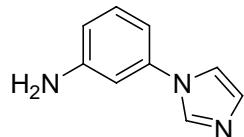
4-Imidazol-1-ylphenol (7l)¹

Following the general procedure, imidazole (0.068g, 1.0mmol) was coupled with 4-bromophenol (0.207 g, 1.2 mmol) in the presence of ligand **4a**. The crude reaction mixture was dissolved in 20 mL of 2 M HCl, and washed once with diethyl ether. The aqueous layer was brought to pH = 8 with Na_2CO_3 , and extracted repeatedly with CH_2Cl_2 . The combined organic layer was dried with anhydrous MgSO_4 , and concentrated under reduced pressure. The crude product was purified over a silica gel column using ethanol/ethyl acetate (1/100) to give a white solid (70% yield). ^1H NMR (600 MHz, CD_3OD): δ 6.89 (d, J = 8.4 Hz, 2H), 7.11 (bs, 1H), 7.33 (d, J = 9.0 Hz, 2H), 7.44 (bs, 1H), 7.97 (bs, 1H) ppm. ^{13}C NMR (150 MHz, CD_3OD): δ 117.3, 120.3, 124.2, 129.7, 130.7, 137.1, 158.5 ppm. GC-MS (EI, m/z): 160 $[\text{M}^+]$.



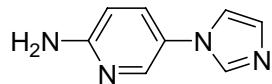
4-Imidazol-1-yl-phenylamine (7m)

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 4-bromoaniline (0.206 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (82% yield). ^1H NMR (600 MHz, CDCl_3): δ 3.58 (bs, 2H), 6.74 (s, 1H), 6.75 (s, 1H), 7.15-7.27 (m, 4H), 7.74 (s, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 115.5, 118.8, 123.3, 128.7, 129.7, 135.8, 146.1 ppm. GC-MS (EI, m/z): 159 [M^+].



3-Imidazol-1-yl-phenylamine (7n)¹

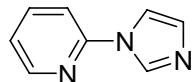
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 3-bromoaniline (131 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a light yellow solid (85% yield). ^1H NMR (400 MHz, CDCl_3): δ 4.00 (bs, 2H), 6.63-6.65 (m, 2H), 6.71-6.73 (m, 1H), 7.17-7.23 (m, 3H), 7.81 (s, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 107.7, 111.1, 113.9, 118.3, 130.0, 130.6, 135.6, 138.3, 148.1 ppm. GC-MS (EI, m/z): 159 [M^+].



5-(1H-Imidazol-1-yl)pyridin-2-amine (7o)

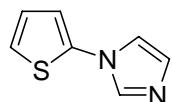
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with

2-amino-5-bromopyridine (0.208 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate to give a light yellow solid (83% yield). ^1H NMR (400 MHz, CDCl_3): δ 4.74 (bs, 2H), 6.57 (d, J = 8.8 Hz, 1H), 7.14 (s, 1H), 7.19 (s, 1H), 7.42 (2d, J = 2.8, 2.4 Hz, 1H), 7.69 (s, 1H), 8.12 (d, J = 2.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 108.7, 119.5, 125.7, 130.3, 132.5, 136.2, 142.1, 158.2 ppm. GC-MS (EI, m/z): 160 [M^+].



2-(1H-imidazolyl)pyridine (7p)²

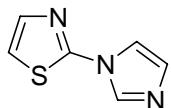
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromopyridine (117 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (98% yield) . ^1H NMR (300 MHz, CDCl_3): δ 7.11 (bs, 1H), 7.14-7.17 (m, 1 H), 7.26 (d, J = 8.2 Hz, 1H), 7.53 (s, 1H), 7.71-7.77 (m, 1H), 8.28 (bs, 1H), 8.39 (2d, J = 1.4, 1.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 112.3, 116.1, 121.5, 122.0, 130.6, 135.0, 139.0, 149.1 ppm. GC-MS (EI, m/z): 145 [M^+].



1-(thiophen-2-yl)-1H-imidazole (7q)⁴

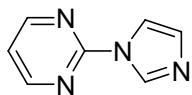
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromothiophene (115 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was

purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (75% yield) . ^1H NMR (400 MHz, CDCl_3): δ 6.94-6.97 (m, 2H), 7.10 (2d, J = 1.6, 2.0 Hz, 1H), 7.13 (s, 1H), 7.16 (t, J = 1.2 Hz, 1H), 7.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 118.9, 120.2, 121.7, 126.3, 130.2, 137.0, 139.1 ppm. GC-MS (EI, m/z): 150 [M $^+$].



1-(thiazol-2-yl)-1H-imidazole (7r)

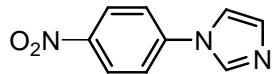
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromothiazole (106 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (85% yield) . ^1H NMR (400 MHz, CDCl_3): δ 7.11-7.14 (m, 2H), 7.47 (t, J = 1.2 Hz, 1H), 7.53 (d, J = 3.6 Hz, 1H), 8.15 (s, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ 115.5, 117.6, 130.8, 135.4, 140.5, 157.4 ppm. GC-MS (EI, m/z): 151 [M $^+$].



2-(1H-imidazol-1-yl)pyrimidine (7s)⁵

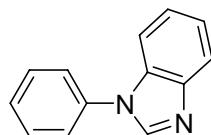
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-chloropyrimidine (137mg, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give white solid (97% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.10 (s, 1H), 7.14 (t, J = 4.8 Hz, 1H), 7.82 (s, 1H), 8.55 (s, 1H), 8.61 (d, J = 5.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 116.4,

118.7, 130.5, 136.0, 158.6 ppm. GC-MS (EI, *m/z*): 146 [M⁺].



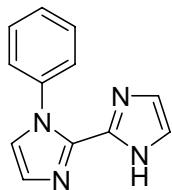
1-(4-Nitrophenyl)-1H-imidazole (7t)²

Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 1-chloro-4-nitrobenzene (0.189 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a pale yellow solid (98% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.30 (s, 1H), 7.39 (s, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 8.04 (s, 1H), 8.39 (d, *J* = 9.0 Hz, 2H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 117.6, 121.0, 125.7, 131.7, 135.4, 141.9, 146.2 ppm. GC-MS (EI, *m/z*): 189 [M⁺].



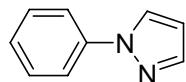
1-Phenyl-1H-benzimidazole (7u)⁶

Following the general procedure, benzimidazole (0.118 g, 1.0 mmol) was coupled with bromobenzene (126 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (75% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.33-7.37 (m, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.52-7.60 (m, 5H), 7.89-7.90 (m, 1H), 8.15 (s, 1H) ppm. ¹³C NMR (150 MHz, CDCl₃): δ 110.4, 120.5, 122.8, 123.6, 124.0, 128.0, 130.0, 133.6, 136.3, 142.2, 143.9 ppm. GC-MS (EI, *m/z*): 194 [M⁺].



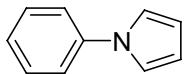
2-(1H-Imidazol-2-yl)-1-phenyl-1H-imidazole (7v)

Following the general procedure, 2-(1H-imidazol-2-yl)-1H-imidazole (0.134 g, 1.0 mmol) was coupled with bromobenzene (126 μ L, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a pale yellow solid (62% yield). 1 H NMR (600 MHz, CDCl₃): δ 7.03 (s, 2H), 7.13 (s, 1H), 7.21 (s, 1H), 7.44-7.46 (m, 2H), 7.48-7.50 (m, 3H) ppm. 13 C NMR (150 MHz, CDCl₃): δ 123.4, 126.3, 127.7, 128.6, 128.9, 138.1, 138.1, 139.2 ppm. GC-MS (EI, *m/z*): 209 [M-1]⁺.



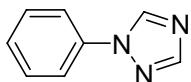
1-Phenyl-1H-pyrazole (7w)⁷

Following the general procedure, 1H-pyrazole (0.068 g, 1.0 mmol) was coupled with bromobenzene (126 μ L, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/8) to give pale yellow oil (87% yield). 1 H NMR (400 MHz, CDCl₃): δ 6.43 (t, *J* = 2.4 Hz, 1H), 7.24-7.28 (m, 1H), 7.39-7.45 (m, 2H), 7.68-7.74 (m, 3H), 7.88 (d, *J* = 2.4 Hz, 1H) ppm; 13 C NMR (75 MHz, CDCl₃): δ 107.6, 119.2, 126.4, 126.8, 129.4, 140.2, 141.1 ppm. GC-MS (EI, *m/z*): 144 [M⁺].



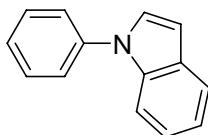
1-Phenyl-1H-pyrrole (7x)⁸

Following the general procedure, 1H-pyrrole (69 μ L, 1.0 mmol) was coupled with bromobenzene (126 μ L, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/10) to give a white solid (72% yield). 1 H NMR (400 MHz, CDCl₃): δ 6.43 (t, J = 2.0 Hz 2H), 7.17 (t, J = 2.0 Hz 2H), 7.26-7.33 (m, 1H), 7.45-7.51 (m, 4H) ppm. 13 C NMR (75 MHz, CDCl₃): δ 110.5, 119.4, 120.6, 125.7, 129.6, 140.9 ppm. GC-MS (EI, *m/z*): 143 [M⁺].



1-Phenyl-1H-1,2,4-triazole (7y)⁸

Following the general procedure, 1,2,4-triazole (0.069 g, 1.0 mmol) was coupled with iodobenzene (134 μ L, 1.2 mmol) at 90 °C in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/2) to give a light yellow solid (96% yield). 1 H NMR (300 MHz, CDCl₃): δ 7.27 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 8.01(bs, 1H), 8.48 (bs, 1H) ppm. 13 C NMR (75 MHz, CDCl₃): δ 119.6, 128.2, 129.7, 137.0, 140.9, 152.6 ppm. GC-MS (EI, *m/z*): 145 [M⁺].



1-Phenyl-1H-indole (7z)⁸

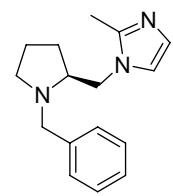
Following the general procedure, 1H-indole (0.117g, 1.0 mmol) was coupled with iodobenzene (134 μ L, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/50) to give colorless oil (98% yield). 1 H NMR (300 MHz, CDCl₃): δ 6.56 (d, *J* = 3.2 Hz, 1H), 7.03-7.13 (m, 2H), 7.18-7.25 (m, 2H), 7.33-7.37 (m, 4H), 7.41-7.60 (m, 2H) ppm. 13 C NMR (75 MHz, CDCl₃): δ 103.7, 110.6, 120.5, 121.3, 122.5, 124.5, 126.5, 128.0, 129.5, 130.1, 136.0, 140.0 ppm. GC-MS (EI, *m/z*): 193 [M⁺].

IV. References

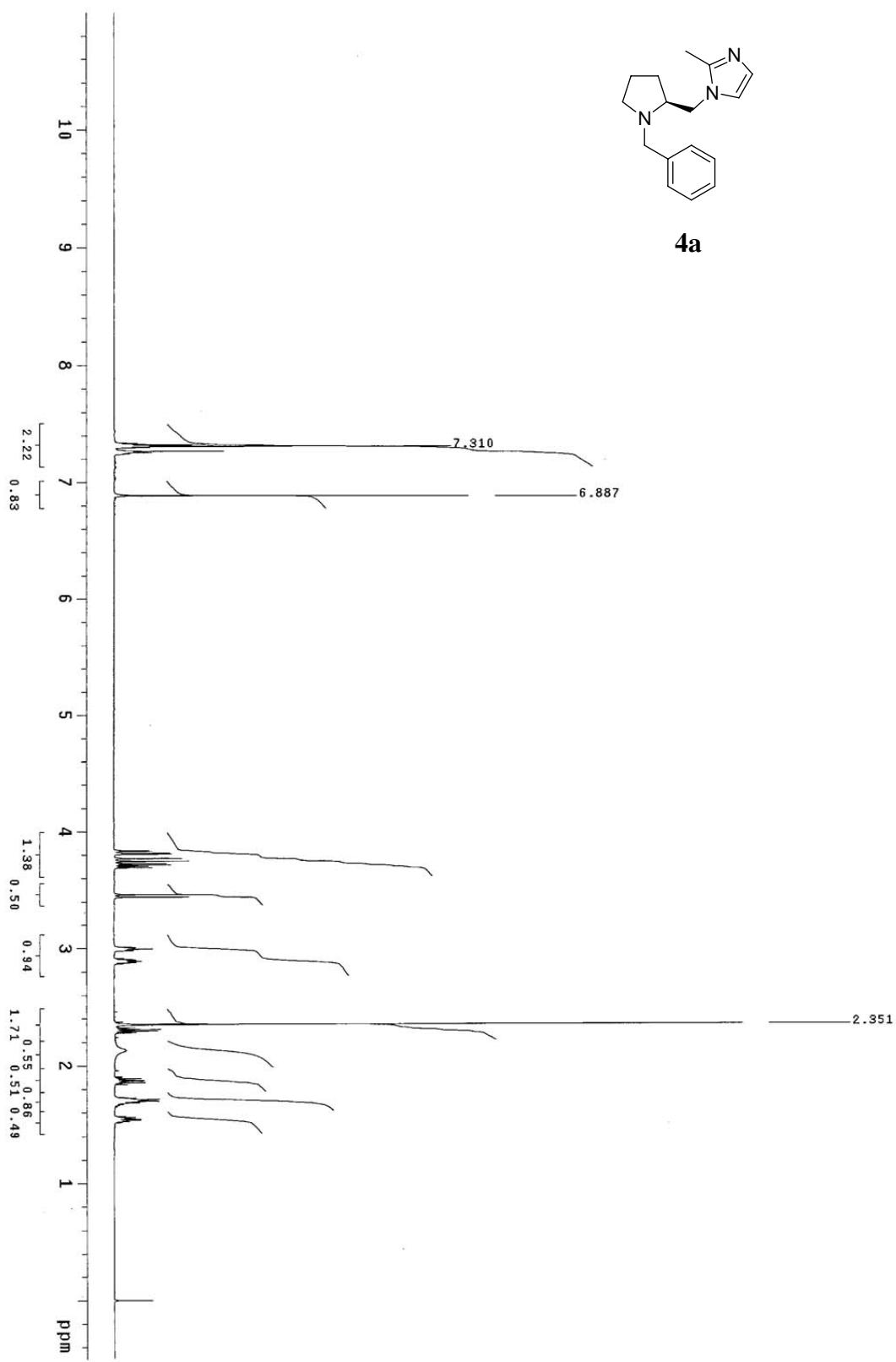
- (1) Altman, R. A.; Buchwald, S. L. *Org. Lett.*, **2006**, 8, 2779-2782.
- (2) Choudary, B. M.; Sridhar, C.; Kantam, M. L.; Venkanna, G. T.; Sreedhar, B. *J. Am. Chem. Soc.* **2005**, 127, 9948-9949.
- (3) Collman, J. P.; Wang, Z.; Zhong, M.; Zeng, L. *J. Chem. Soc., Perkin Trans. 1*, **2000**, 1217-1221.
- (4) Lv, X.; Wang, Z.; Bao, W. *Tetrahedron* **2006**, 62, 4756-4761.
- (5) Xie, Y.; Pi, S; Wang, J; Yin, D.; Li, J. *J. Org. Chem.* **2006**, 71, 8324-8327.
- (6) Nishiura, K.; Urawa, Y.; Sodab, S. *Adv. Synth. Catal.* **2004**, 346, 1679-1684.
- (7) Cristau, H. J.; Cellier, P. P.; Spindler, J. F.; Taillefer, M. *Eur. J. Org. Chem.* **2004**, 695-709.
- (8) Cristau, H. J.; Cellier, P. P.; Spindler, J. F.; Taillefer, M. *Chem.-Eur. J.* **2004**, 10, 5607-5622.

V. Copies of 1 H and 13 C NMR spectra for compounds **4a-4c**, **3a-3b**, **2a-2b** and **7a-z**

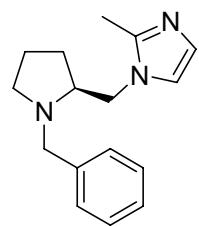
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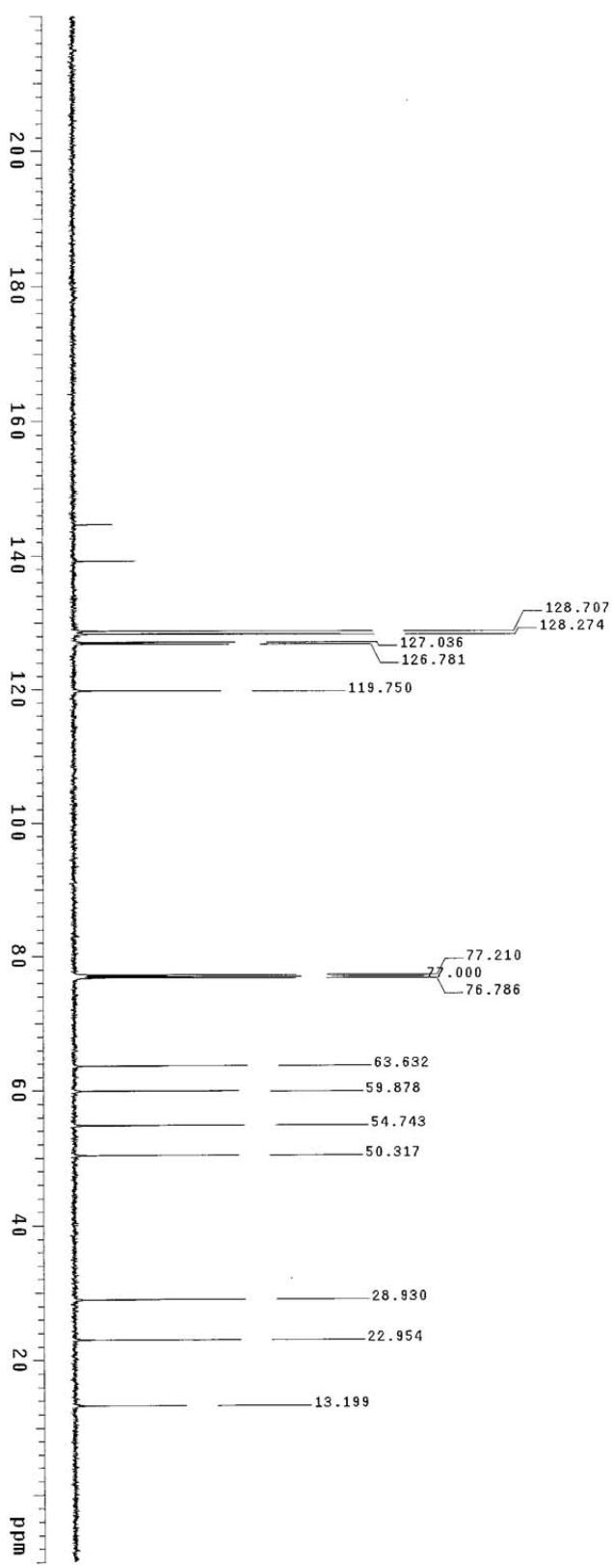
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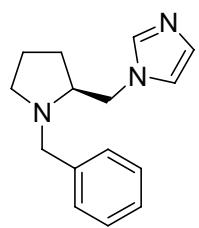
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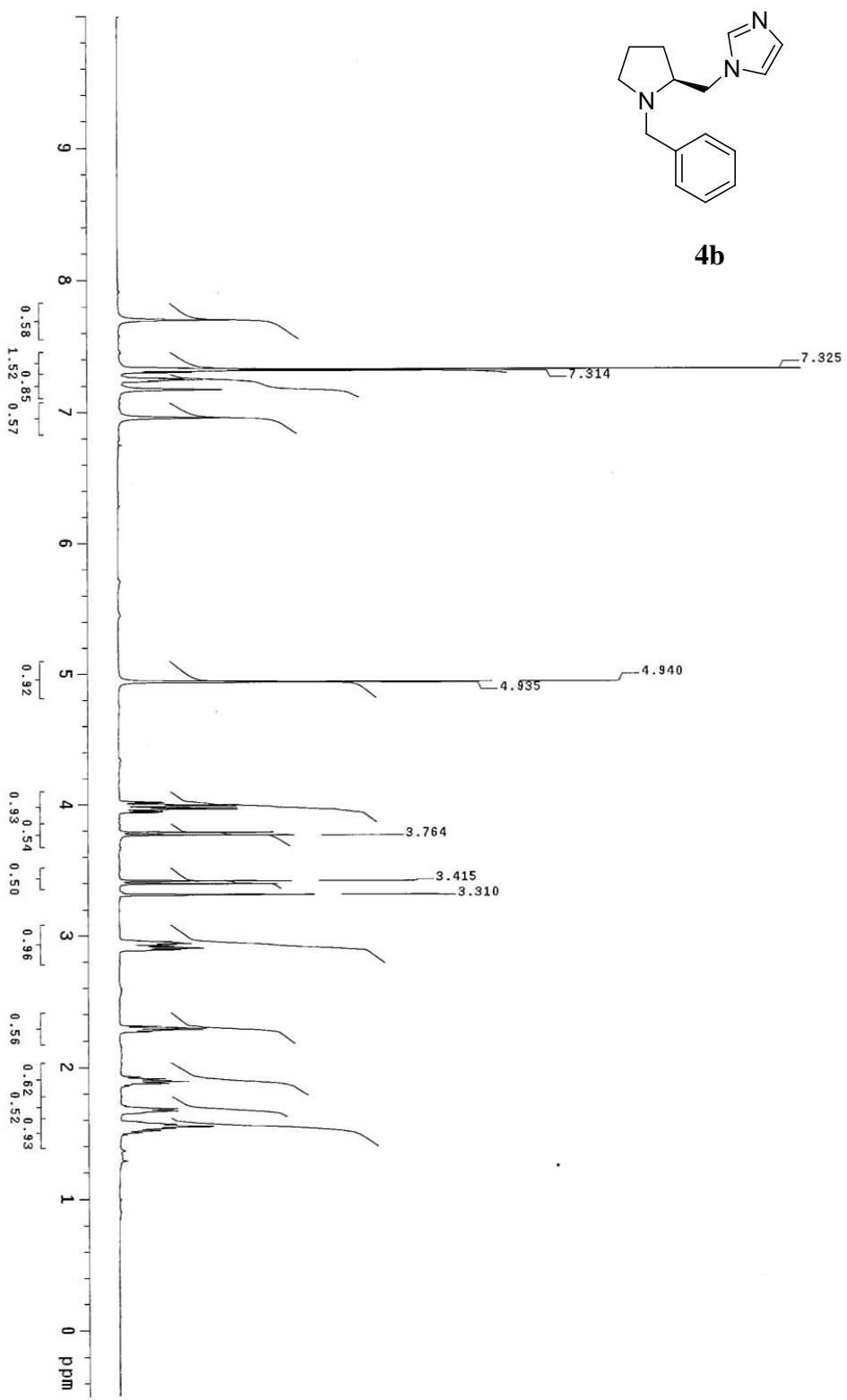
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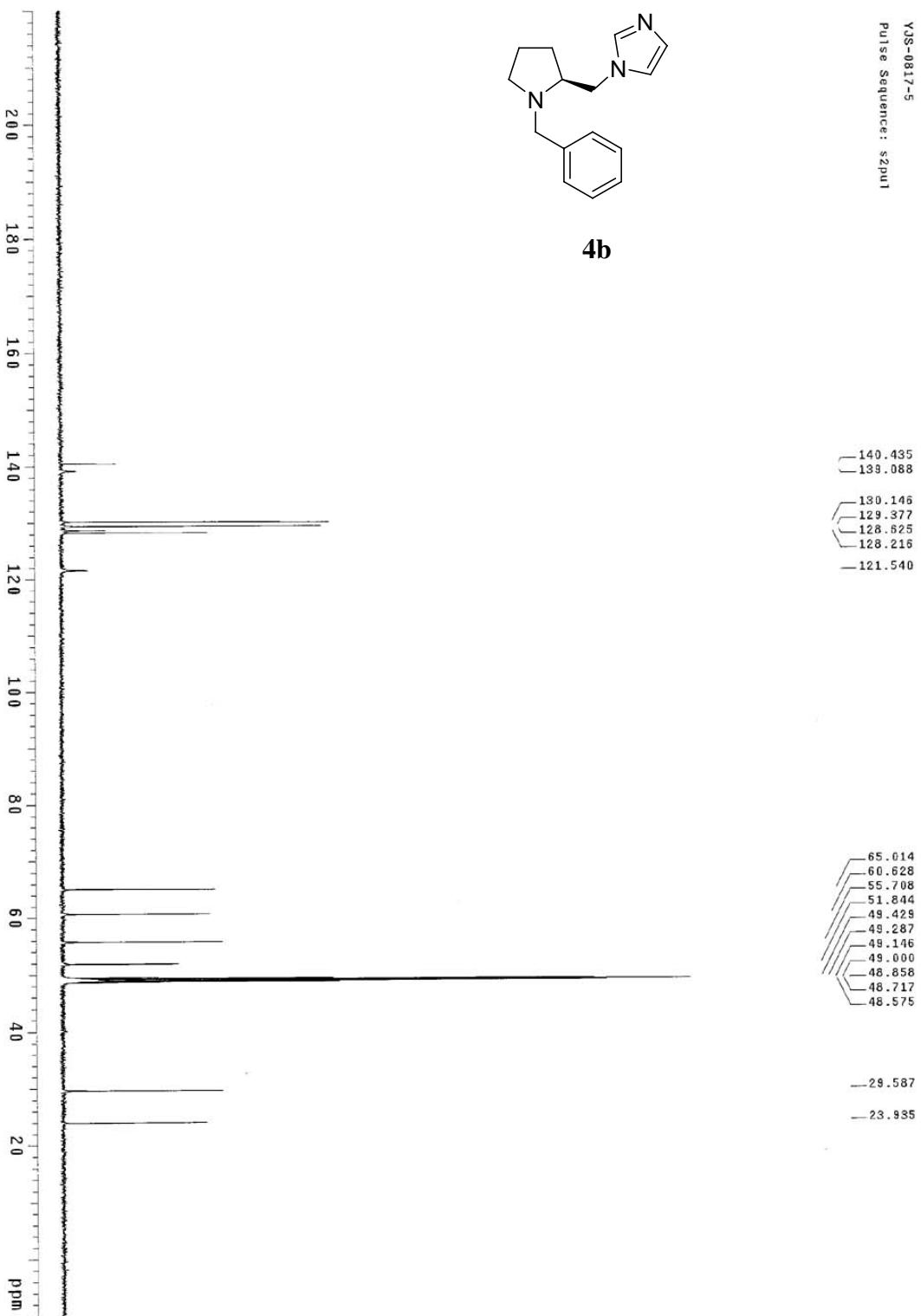


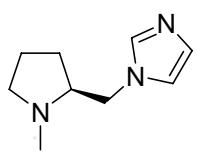
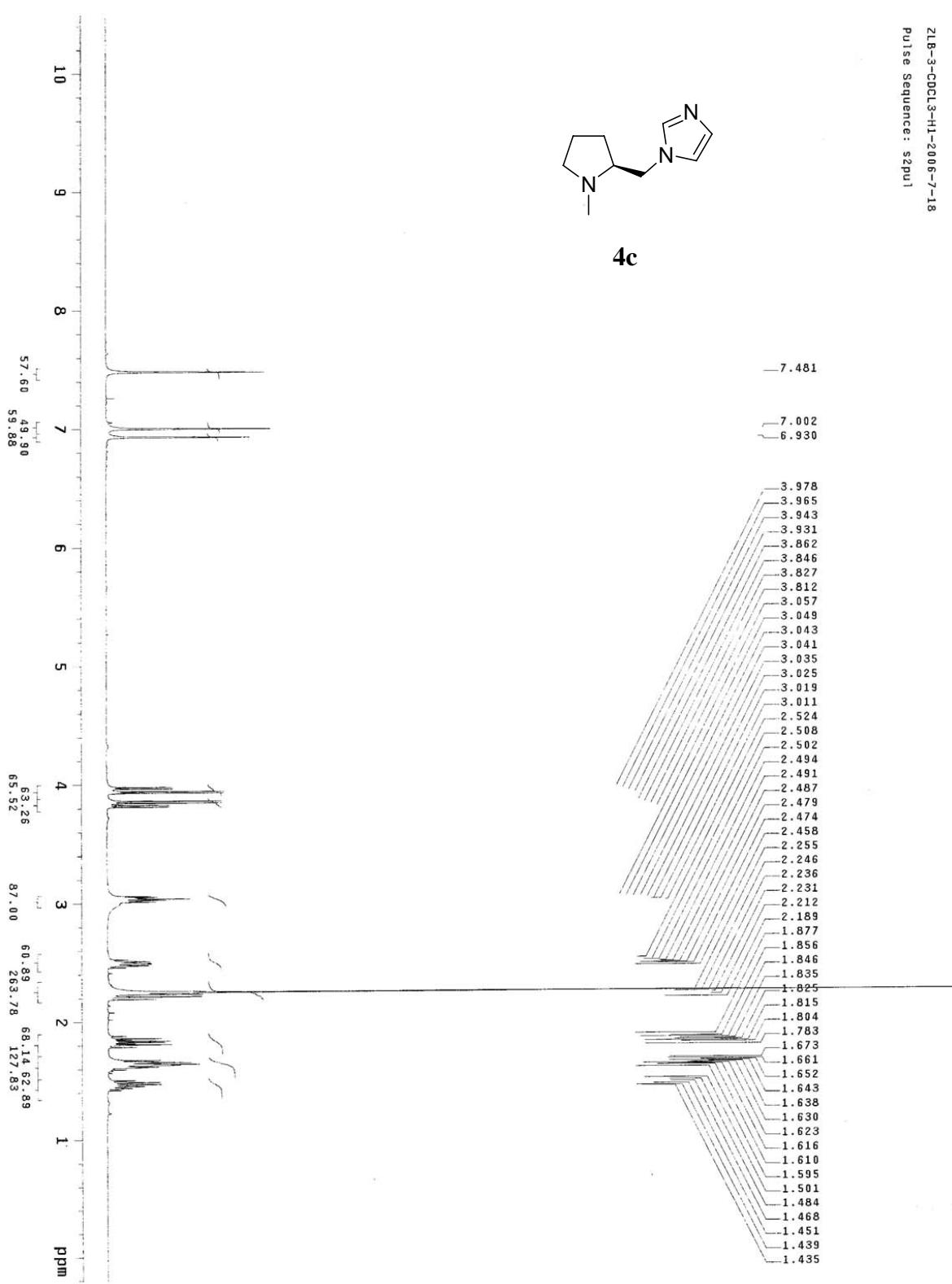
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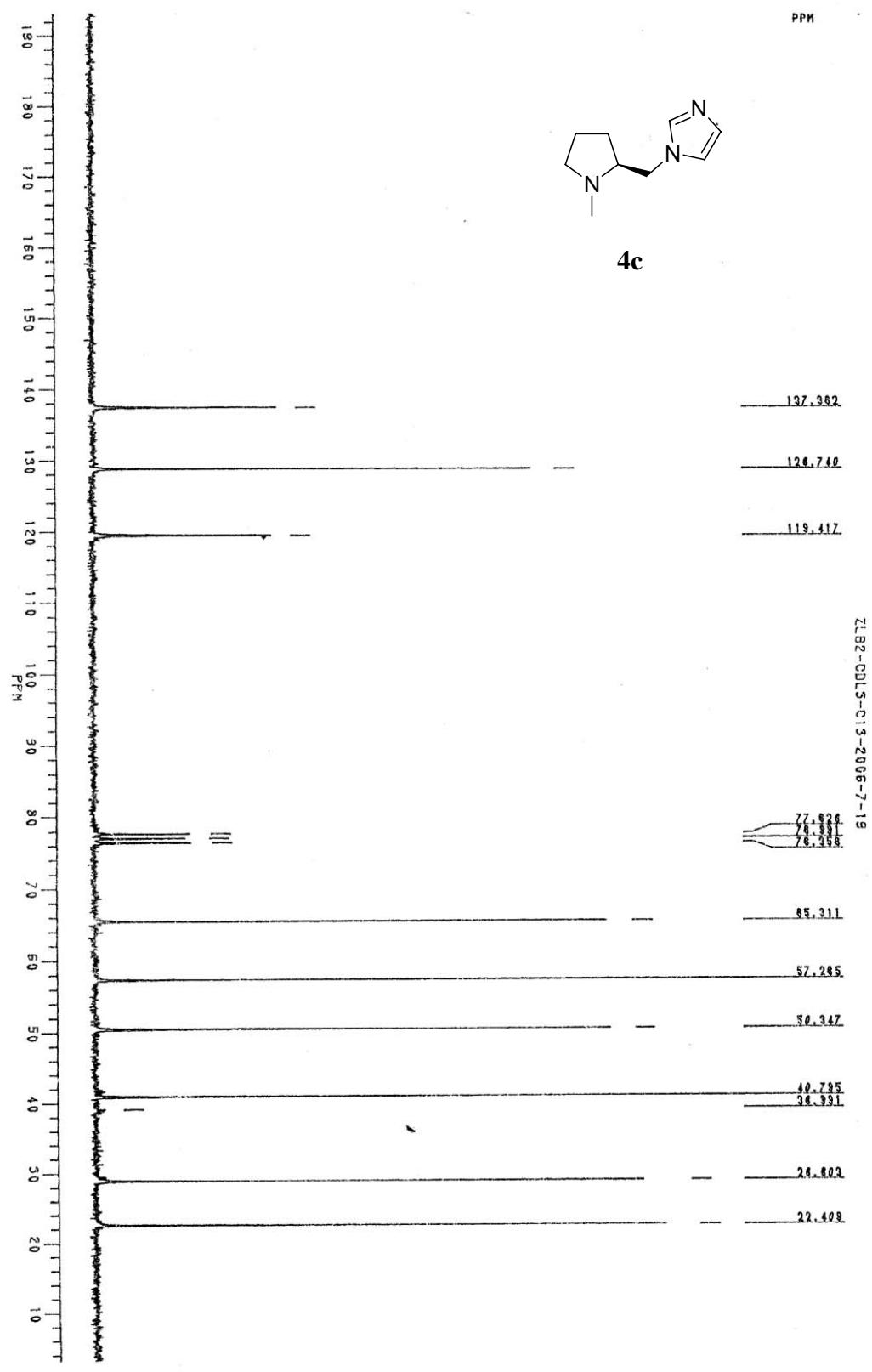


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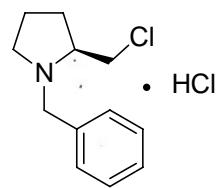




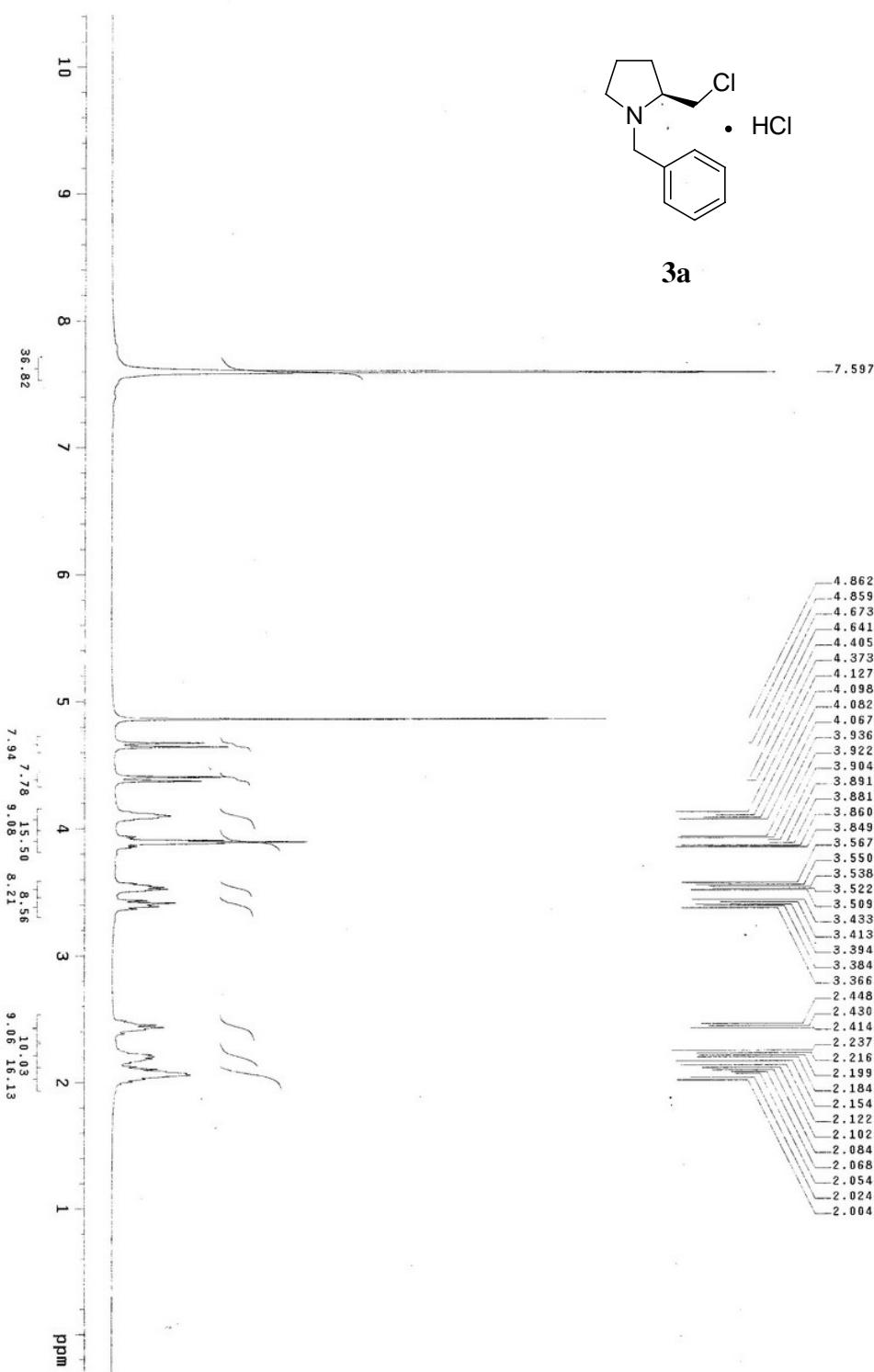
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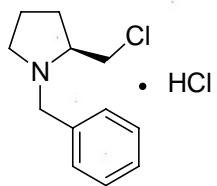
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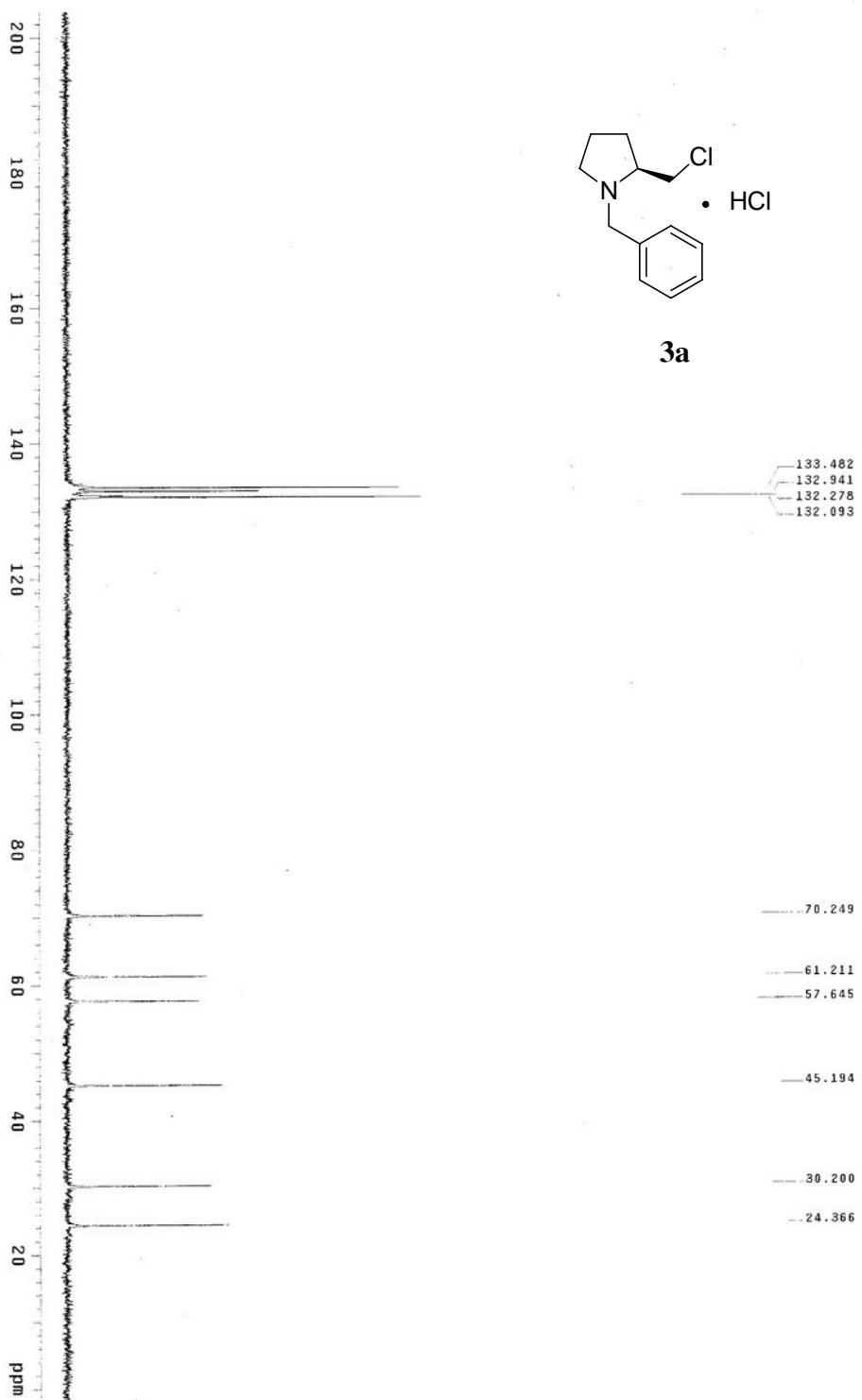
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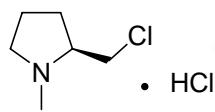
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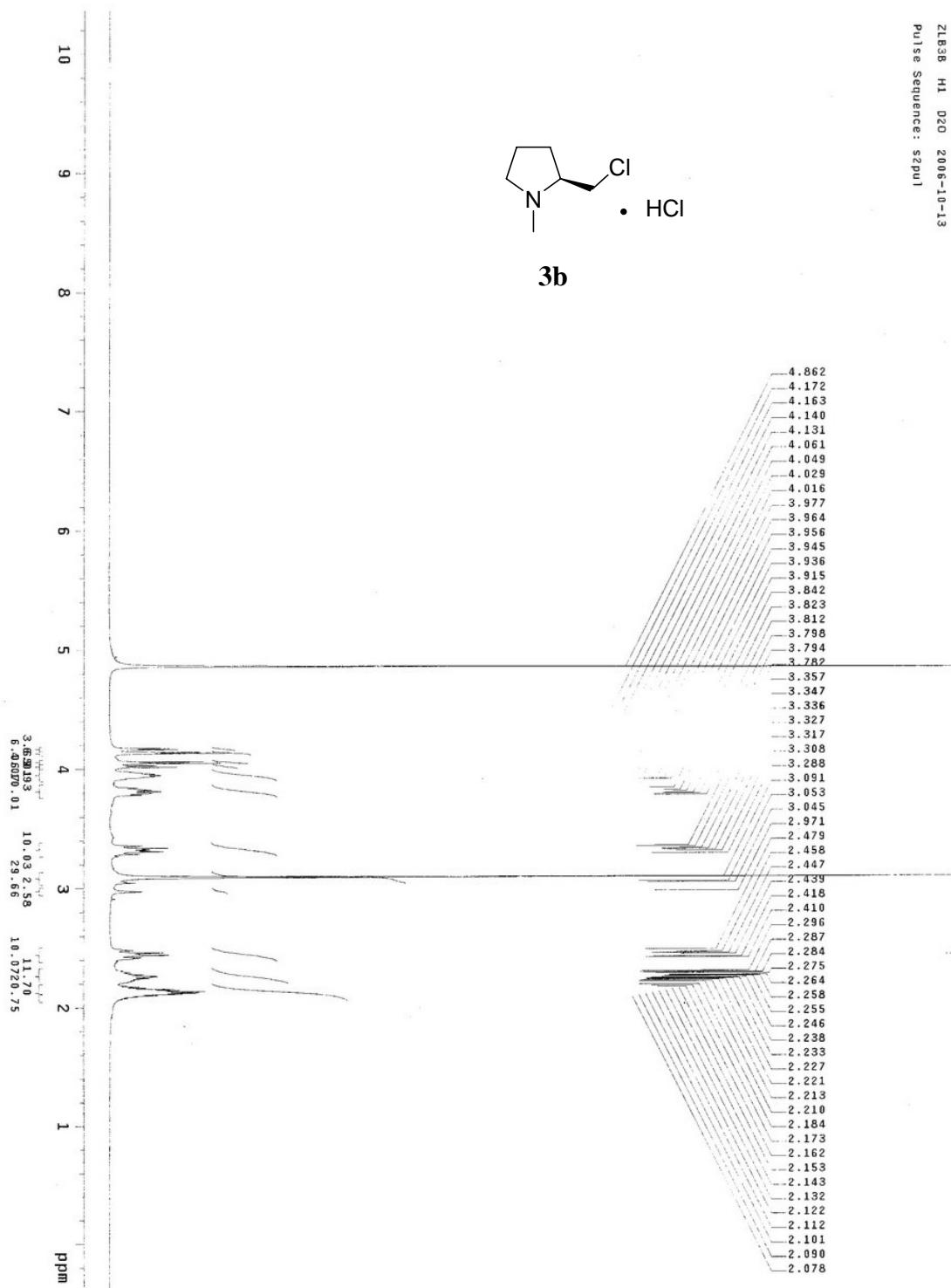
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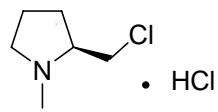


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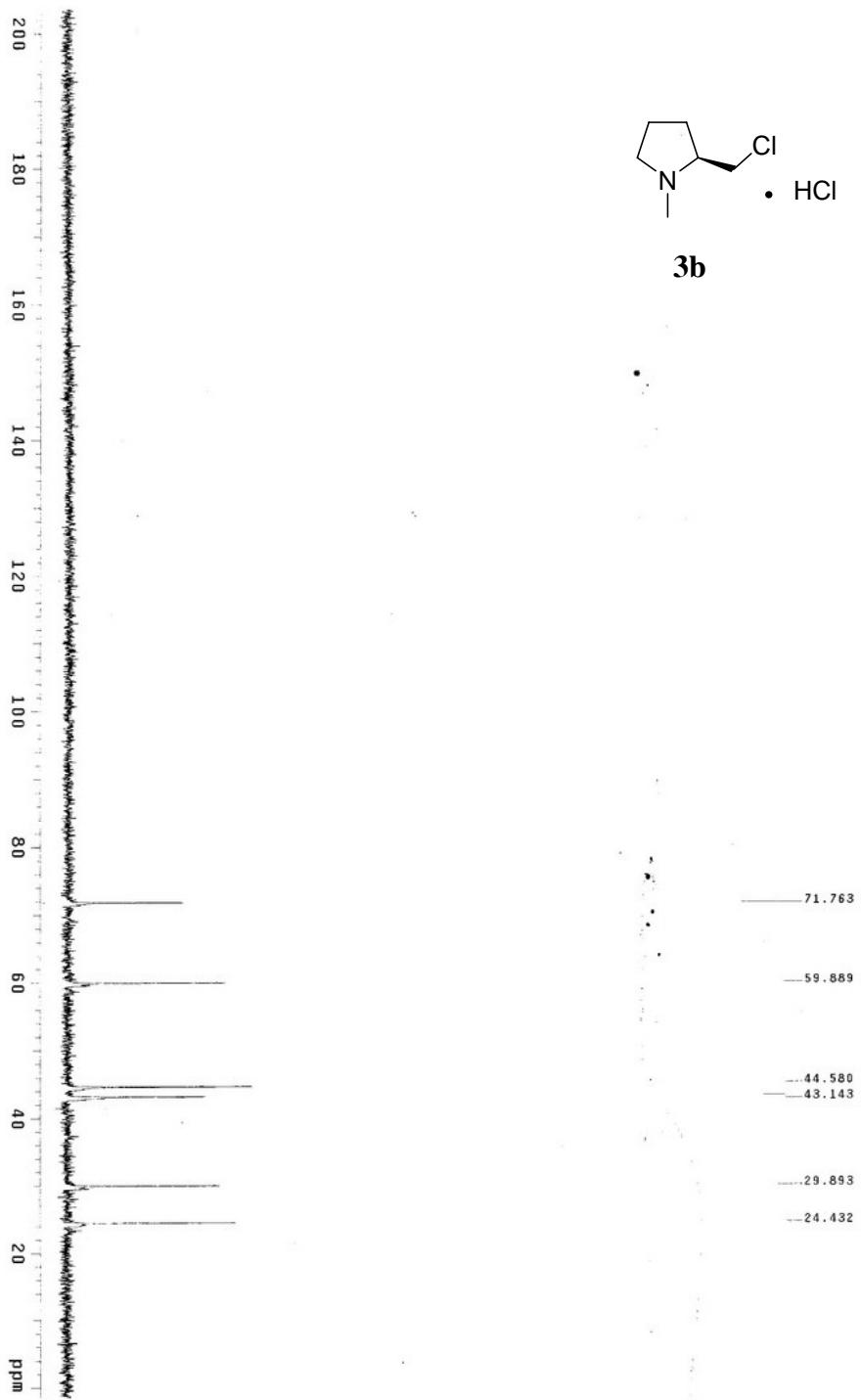


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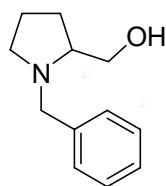




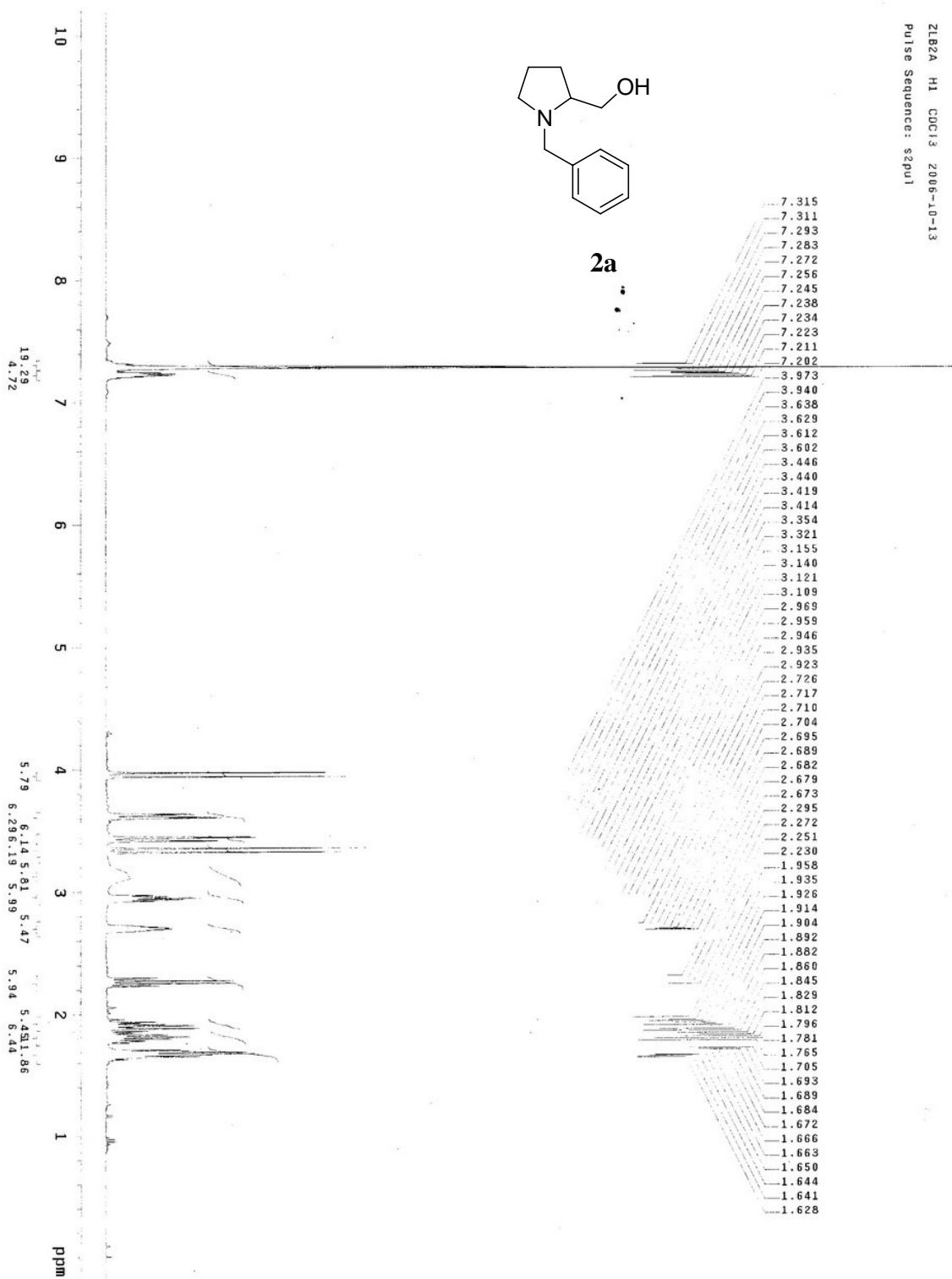
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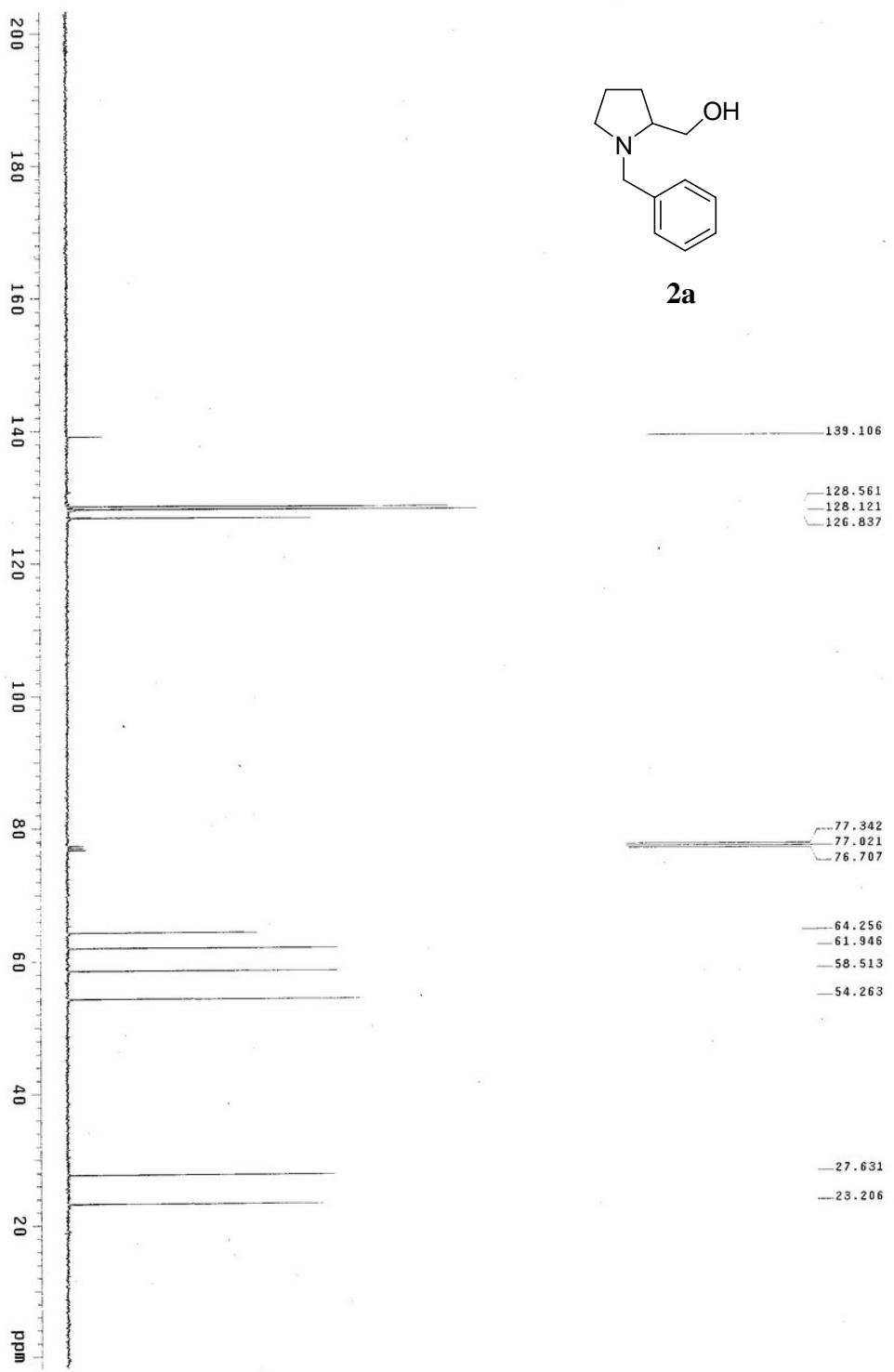


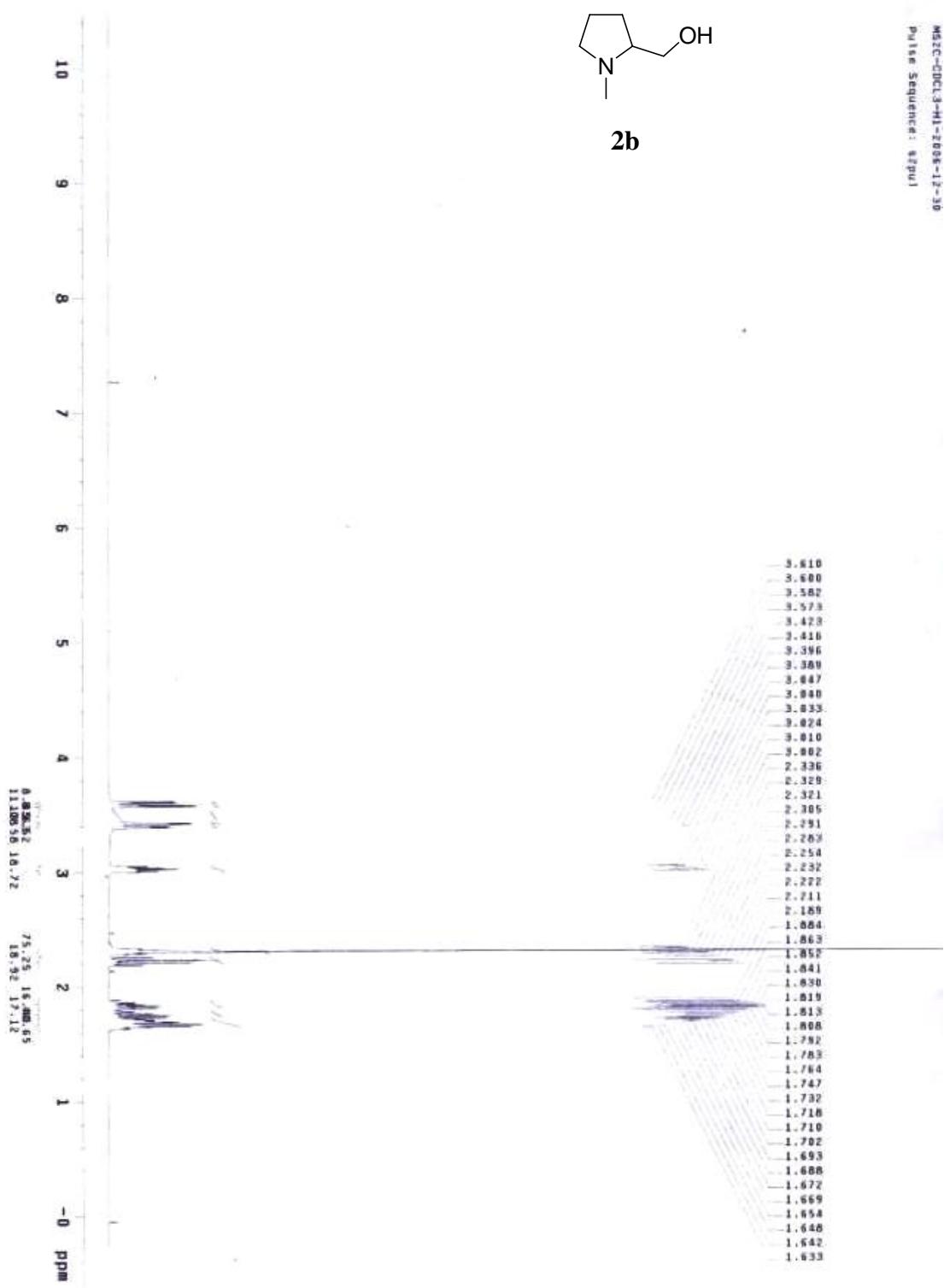
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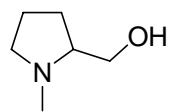
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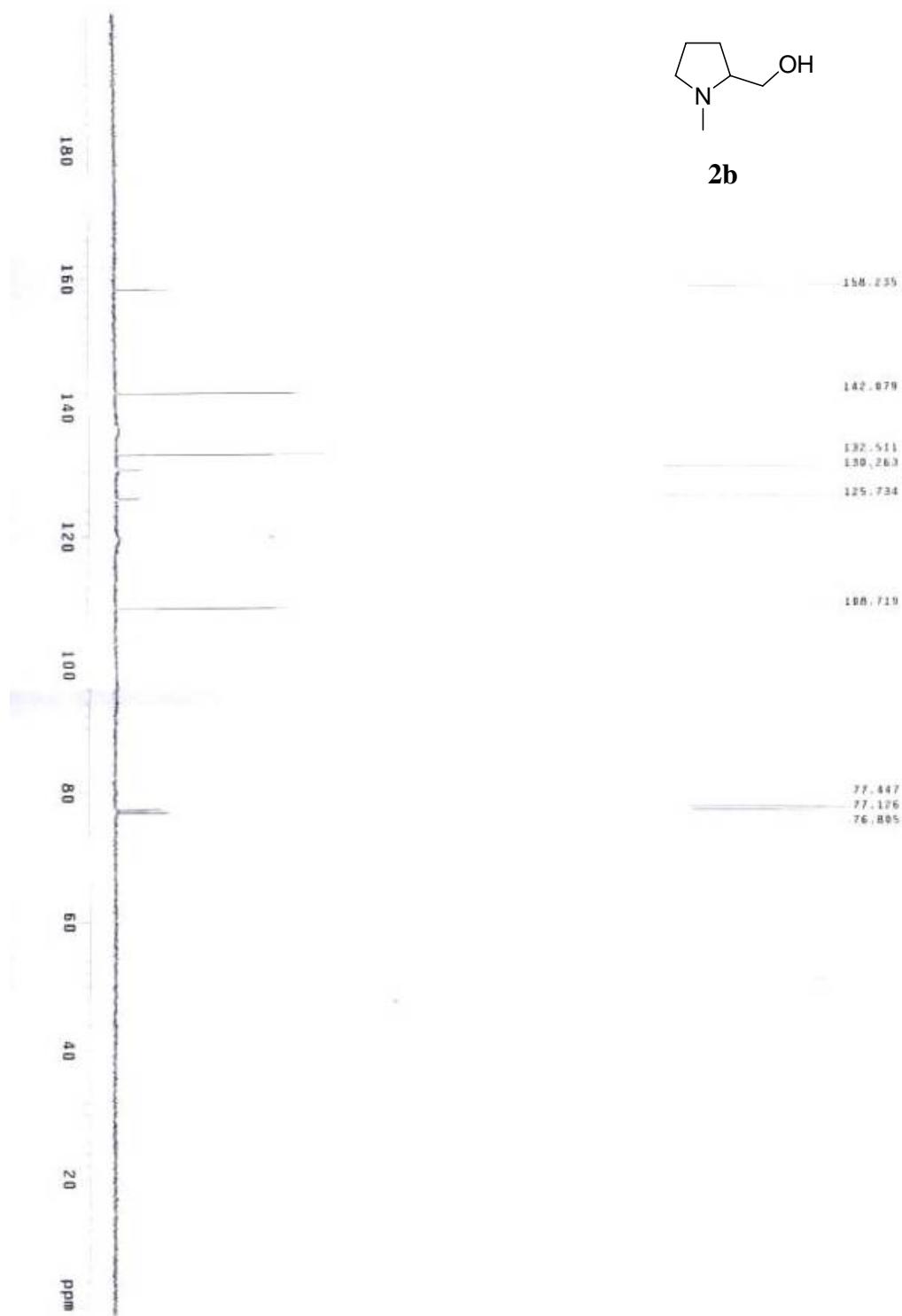




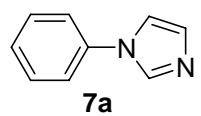
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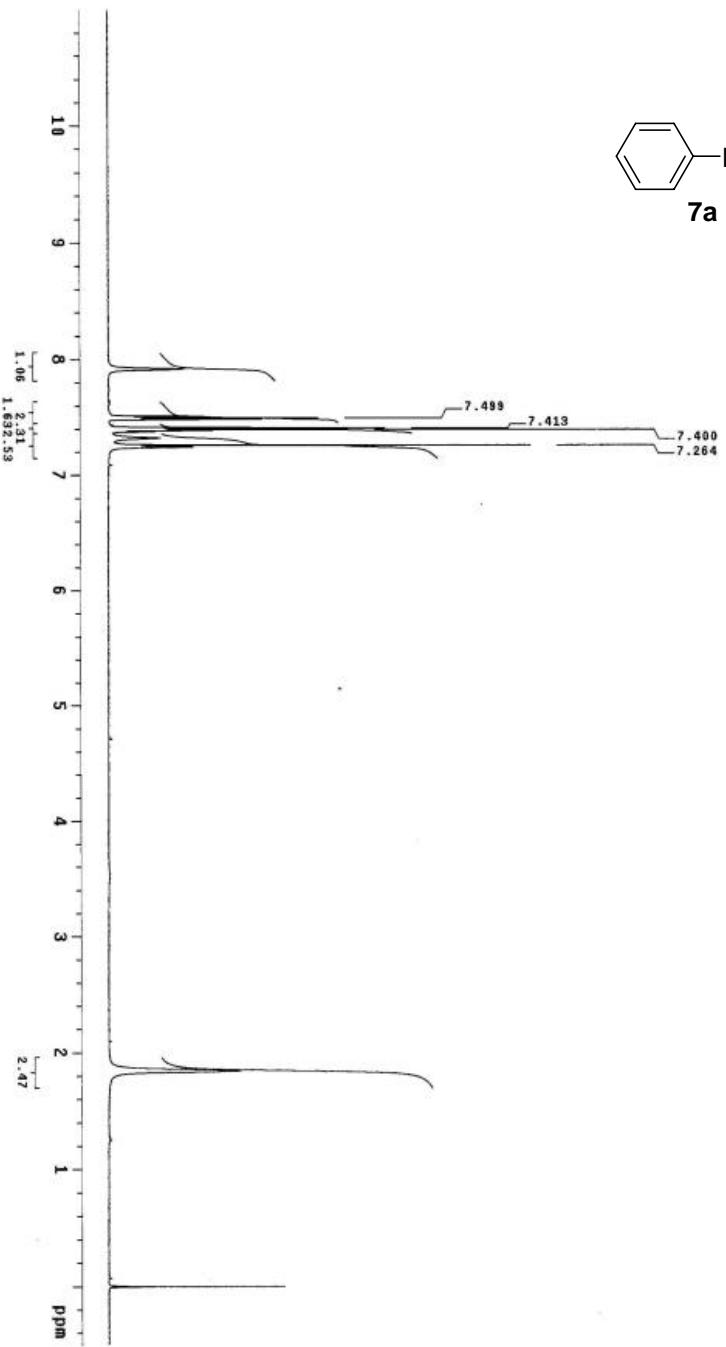
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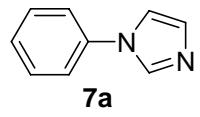
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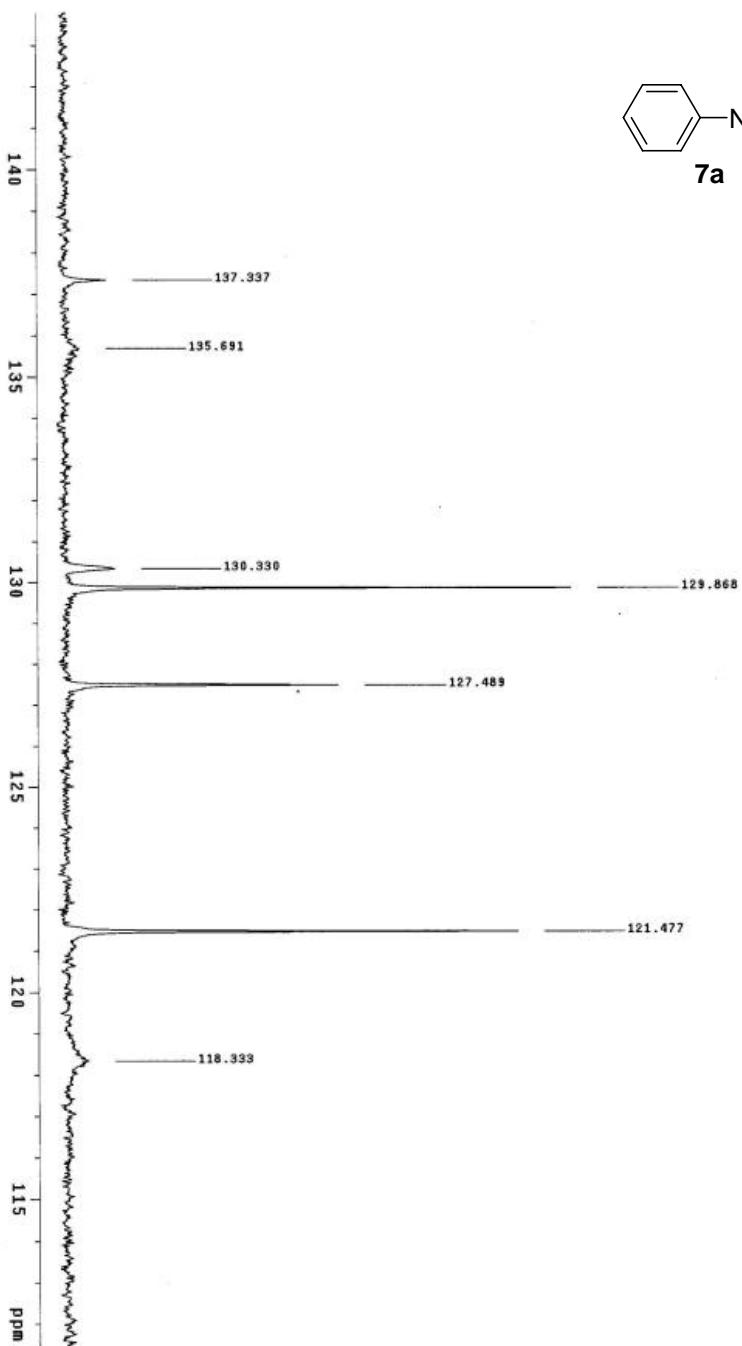
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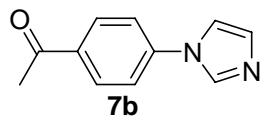


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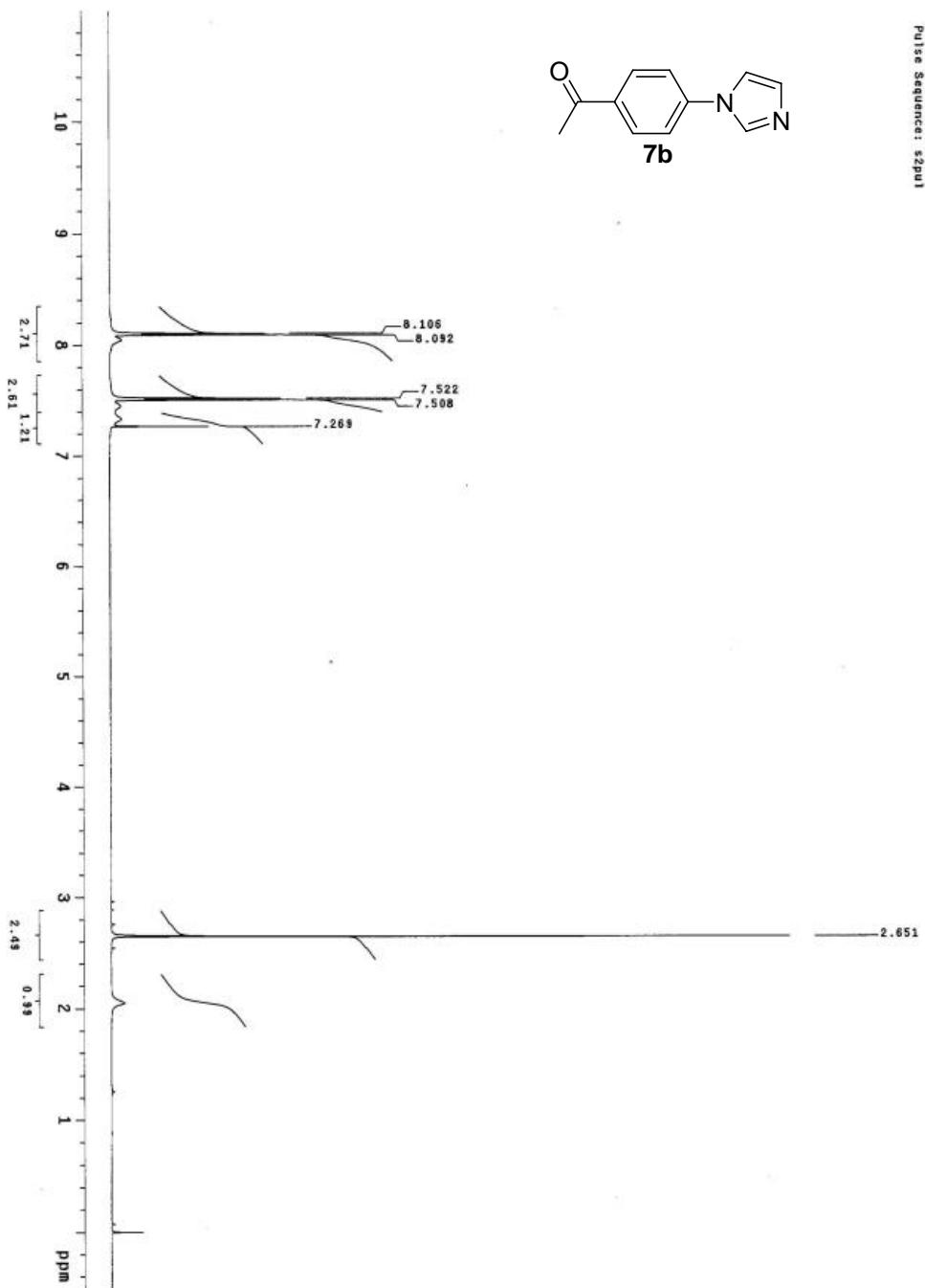


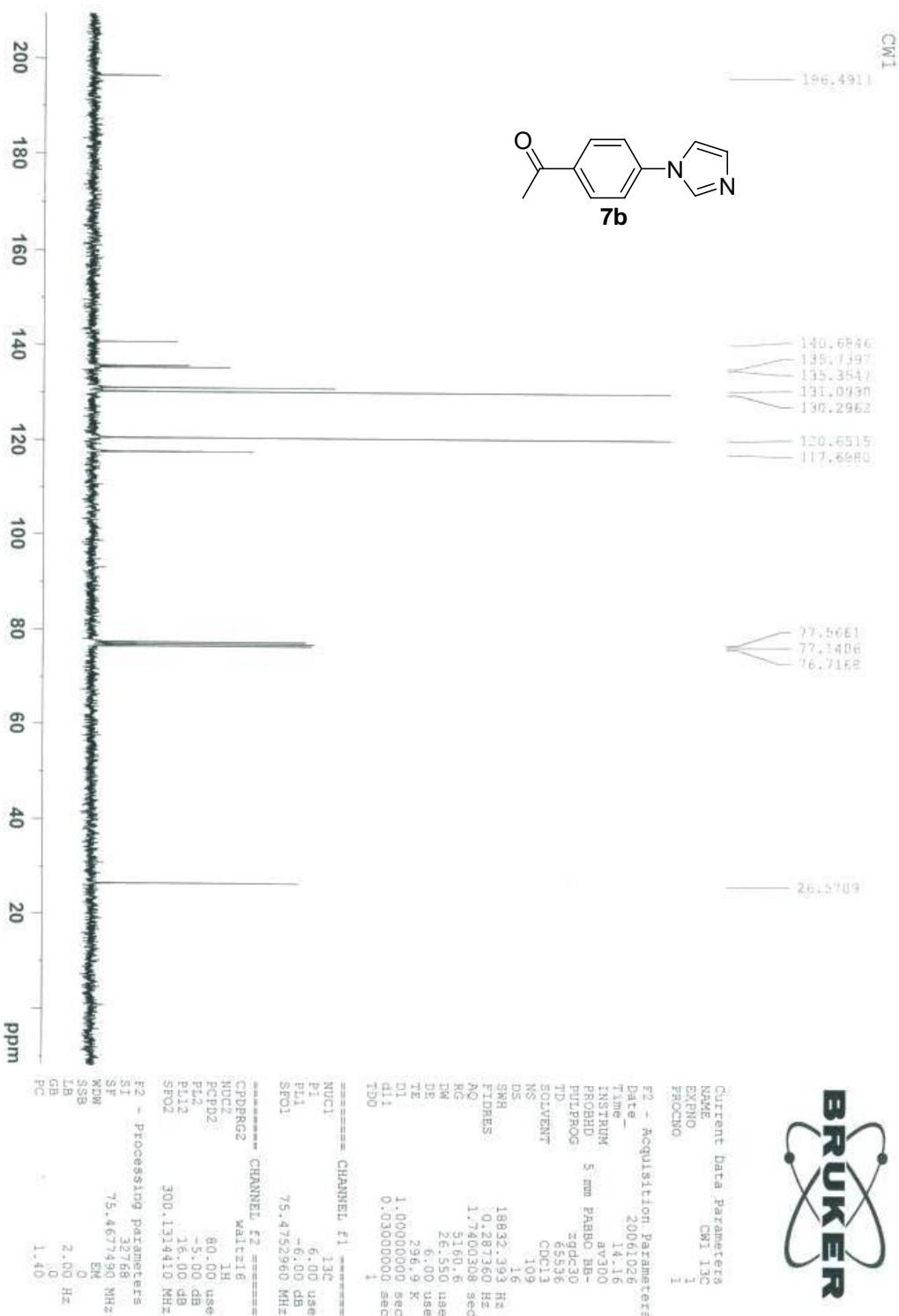
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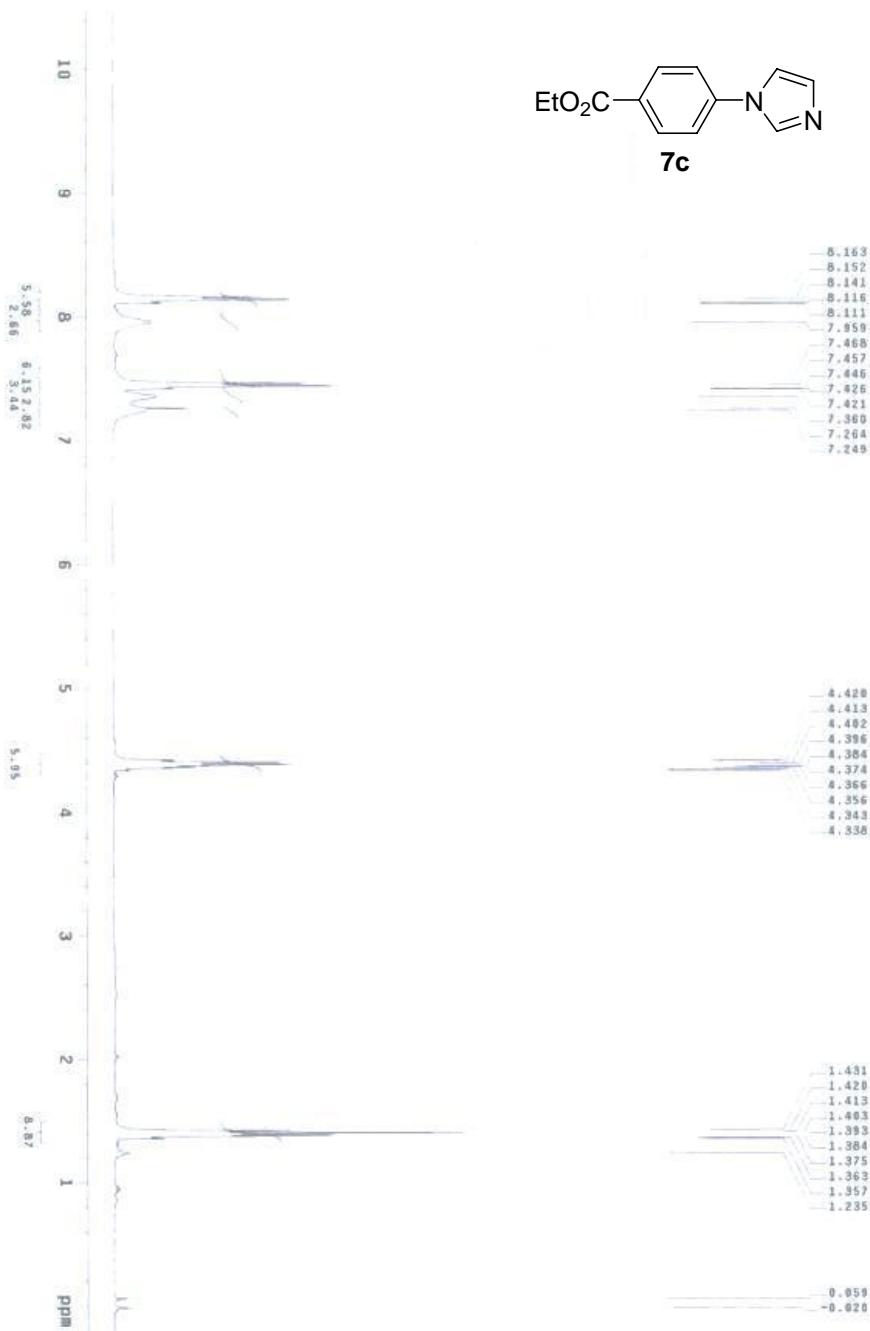


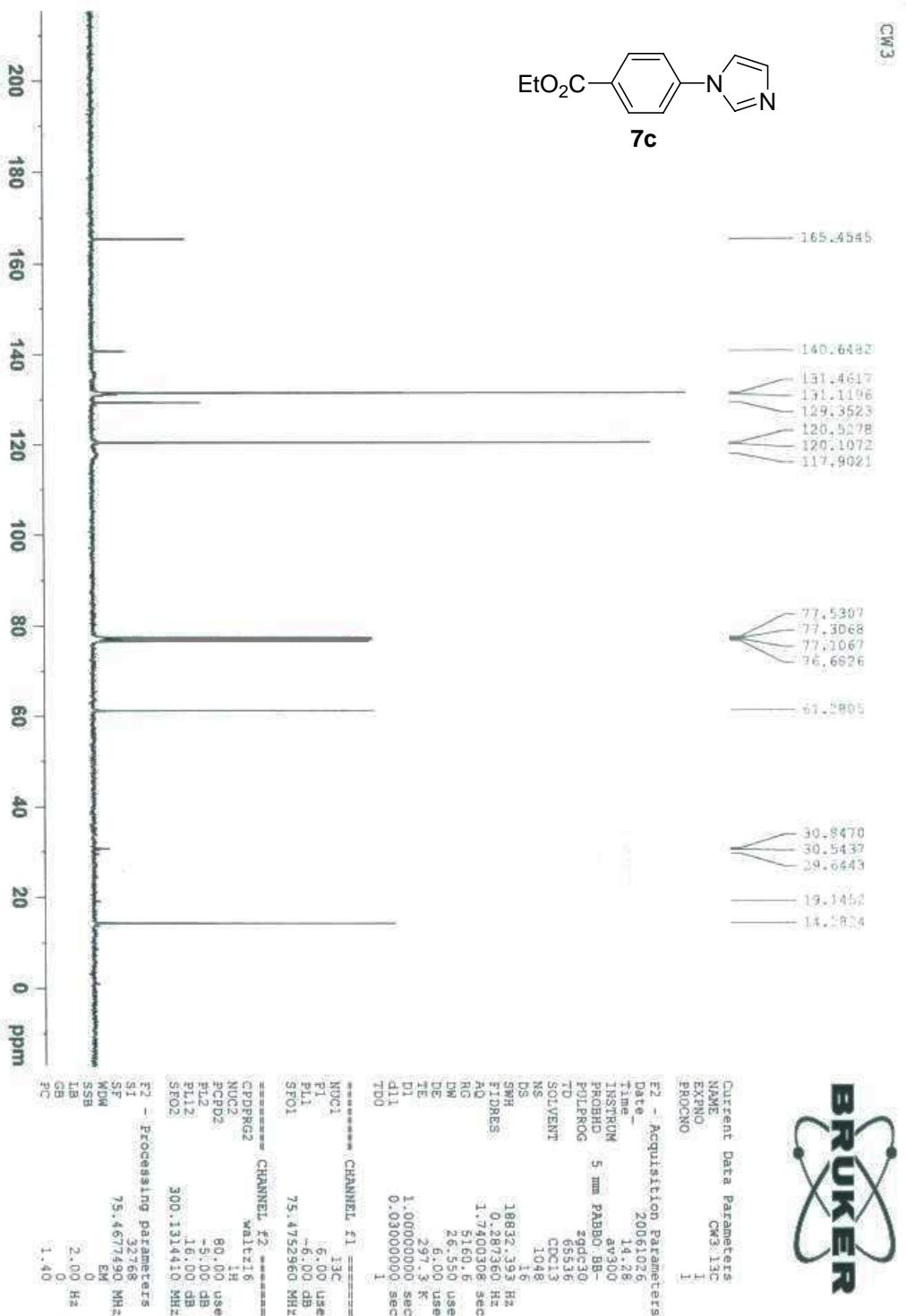


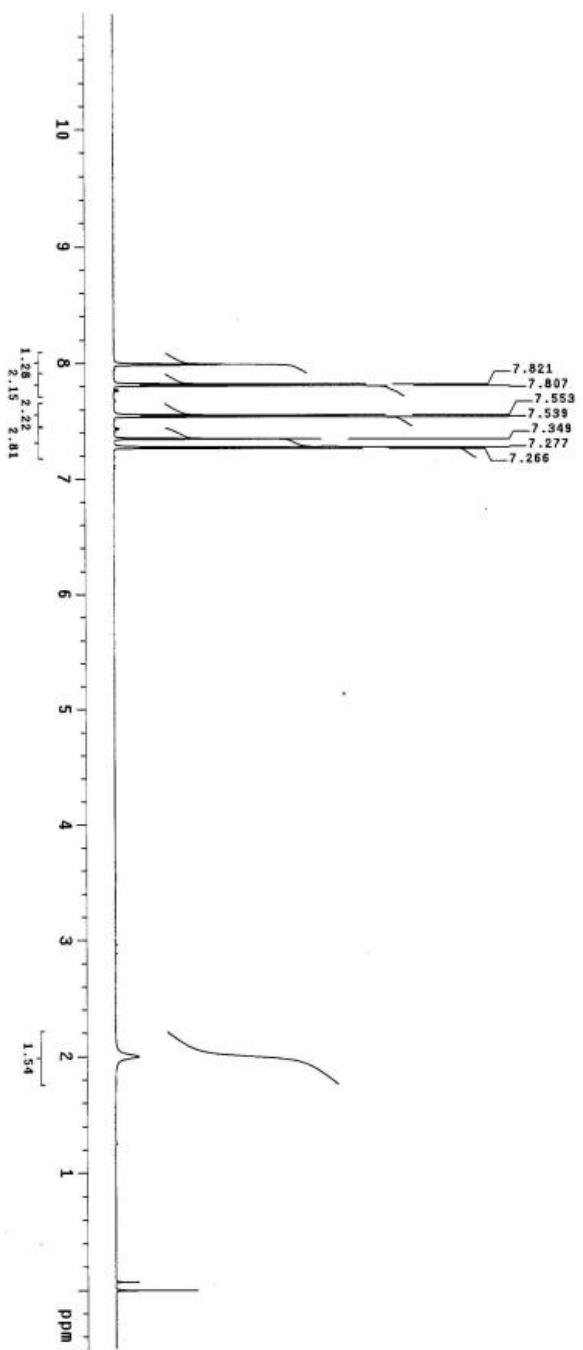
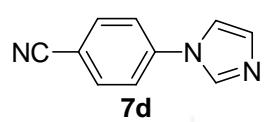


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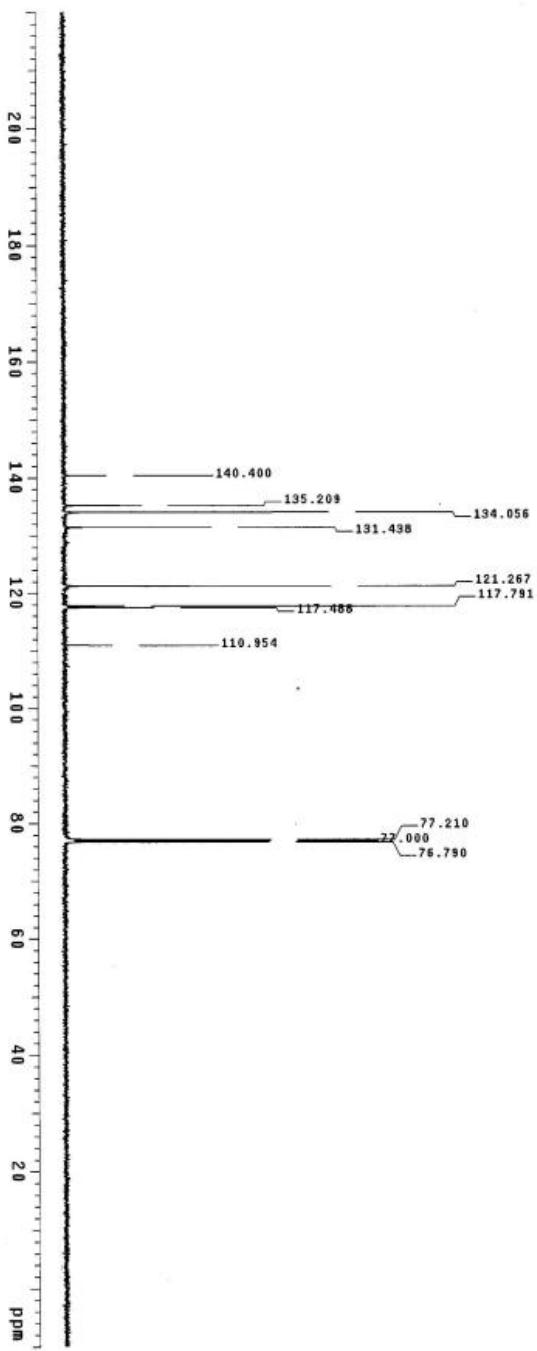
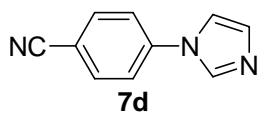
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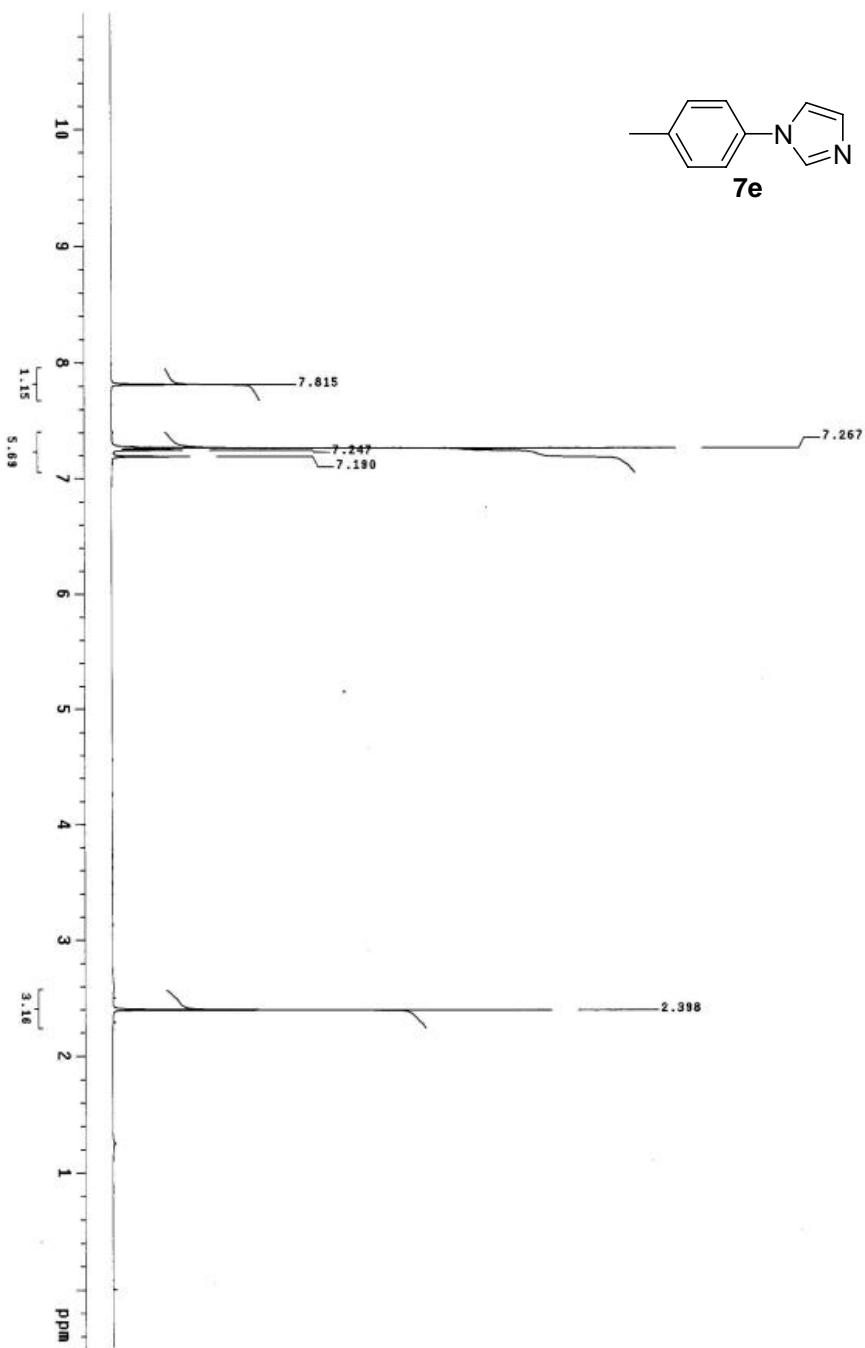


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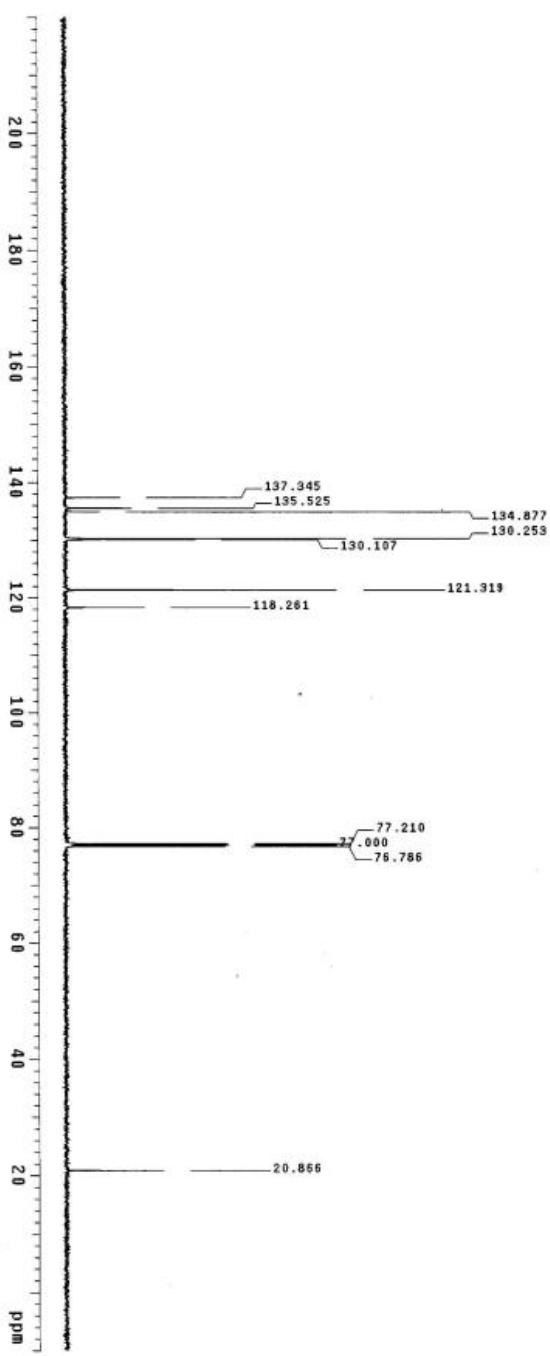


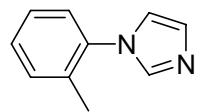
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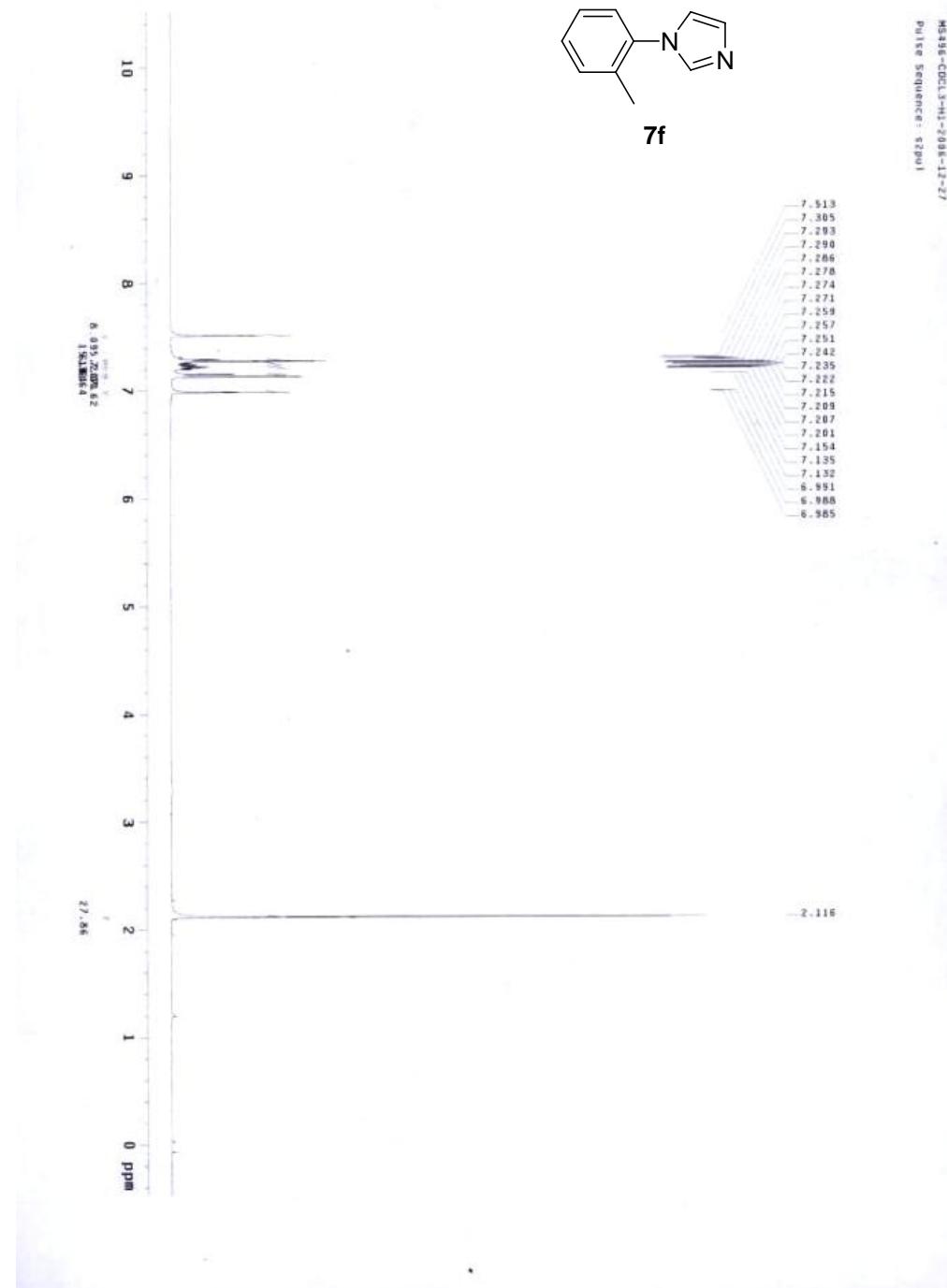


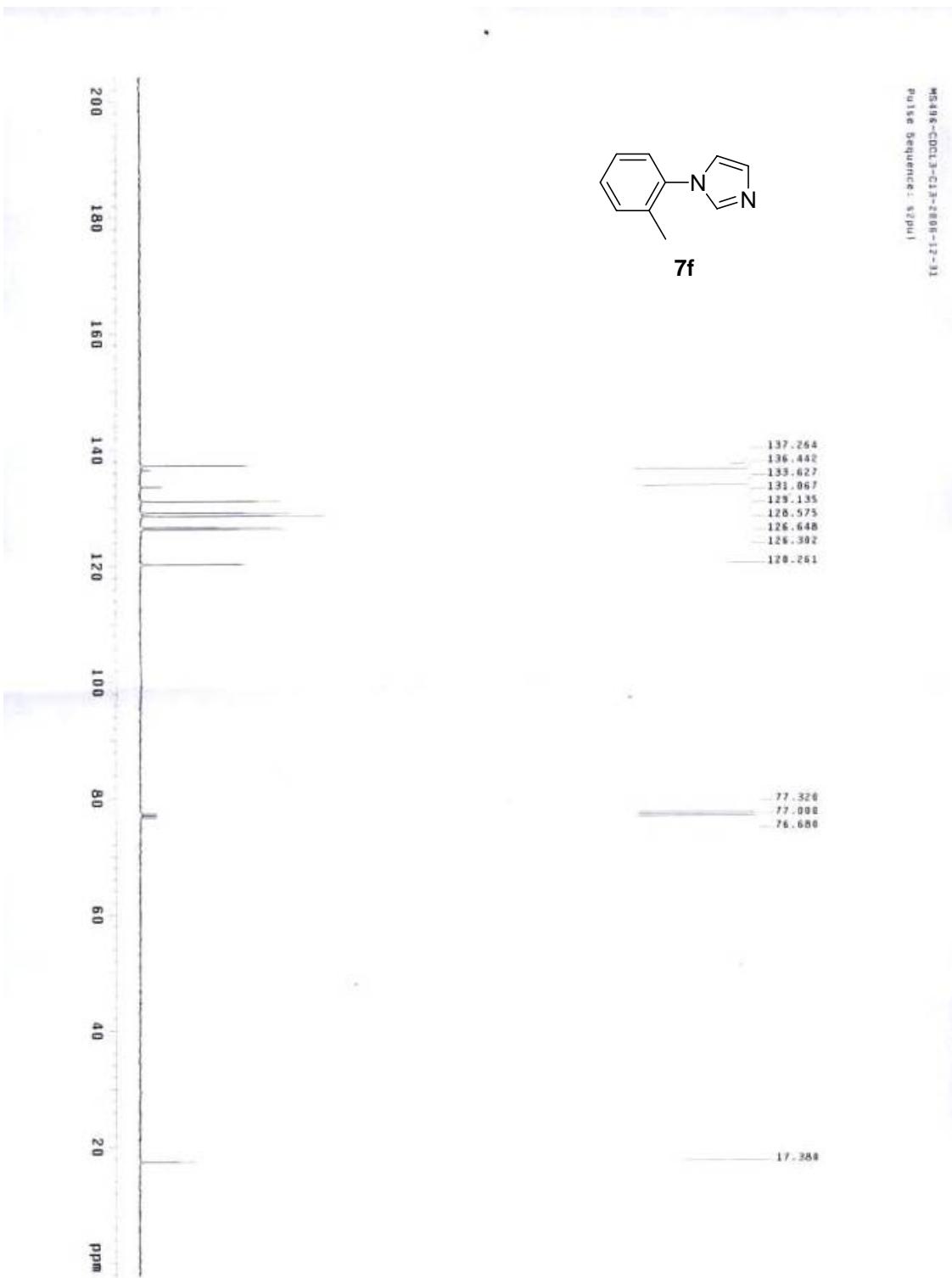
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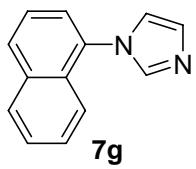




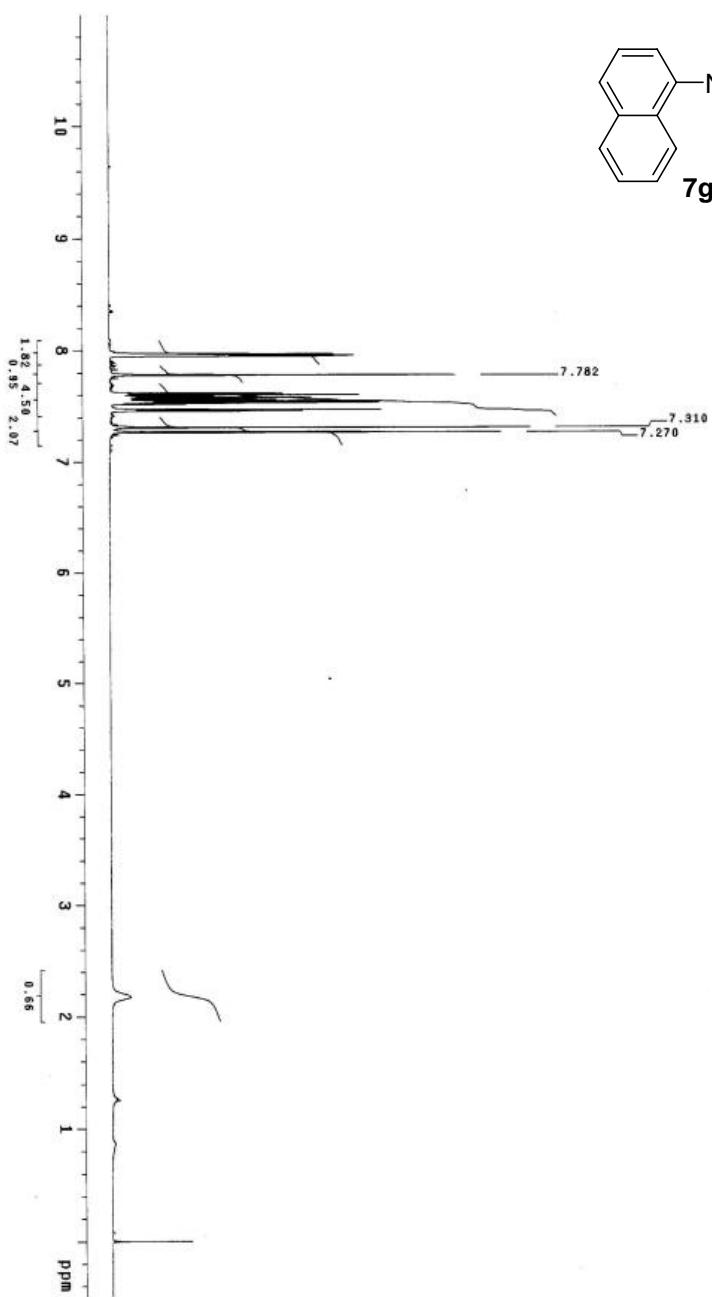
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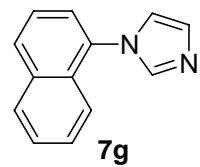
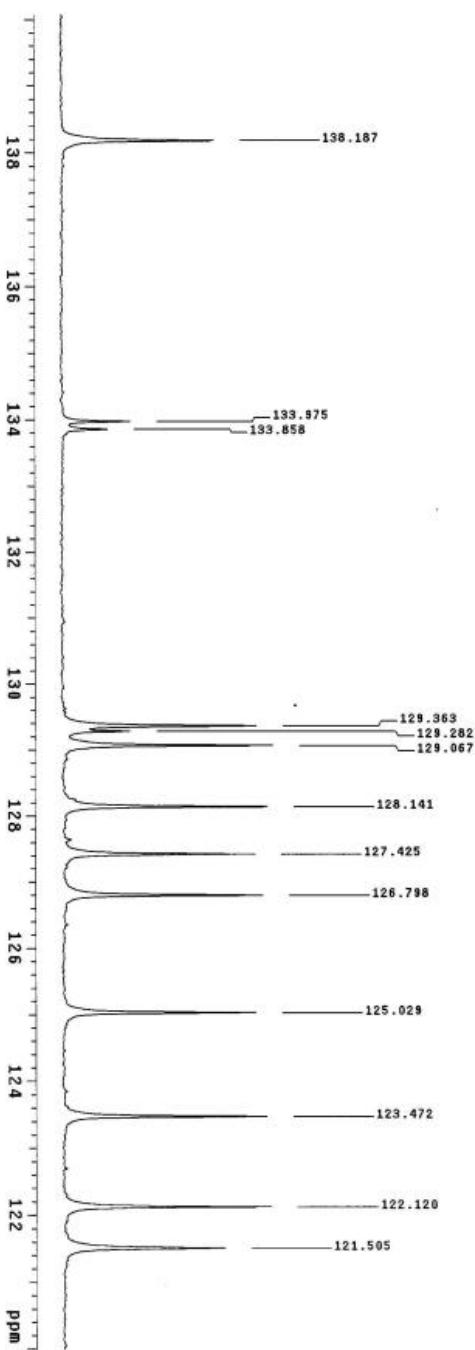






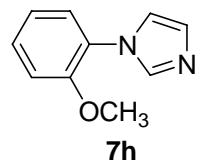
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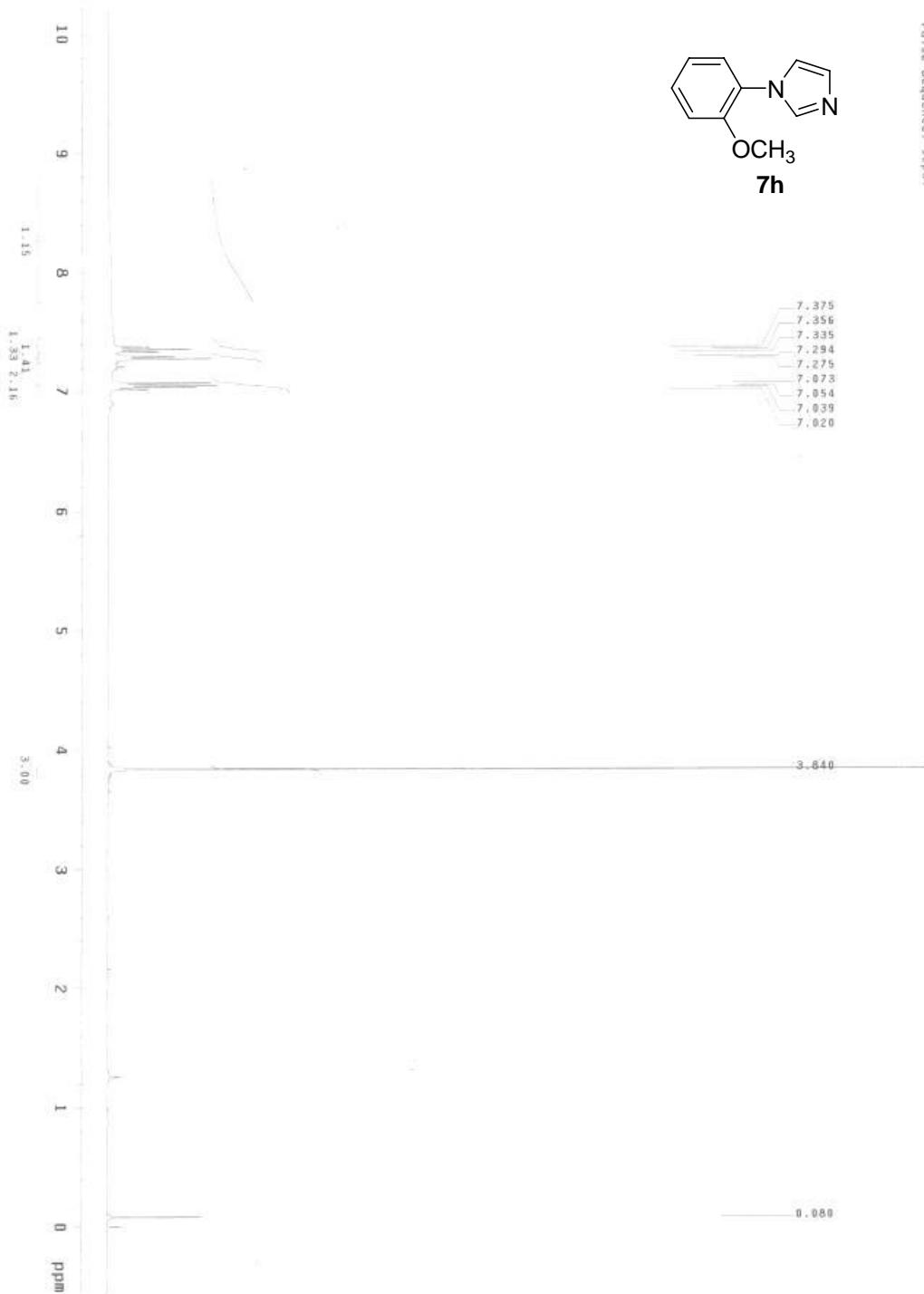


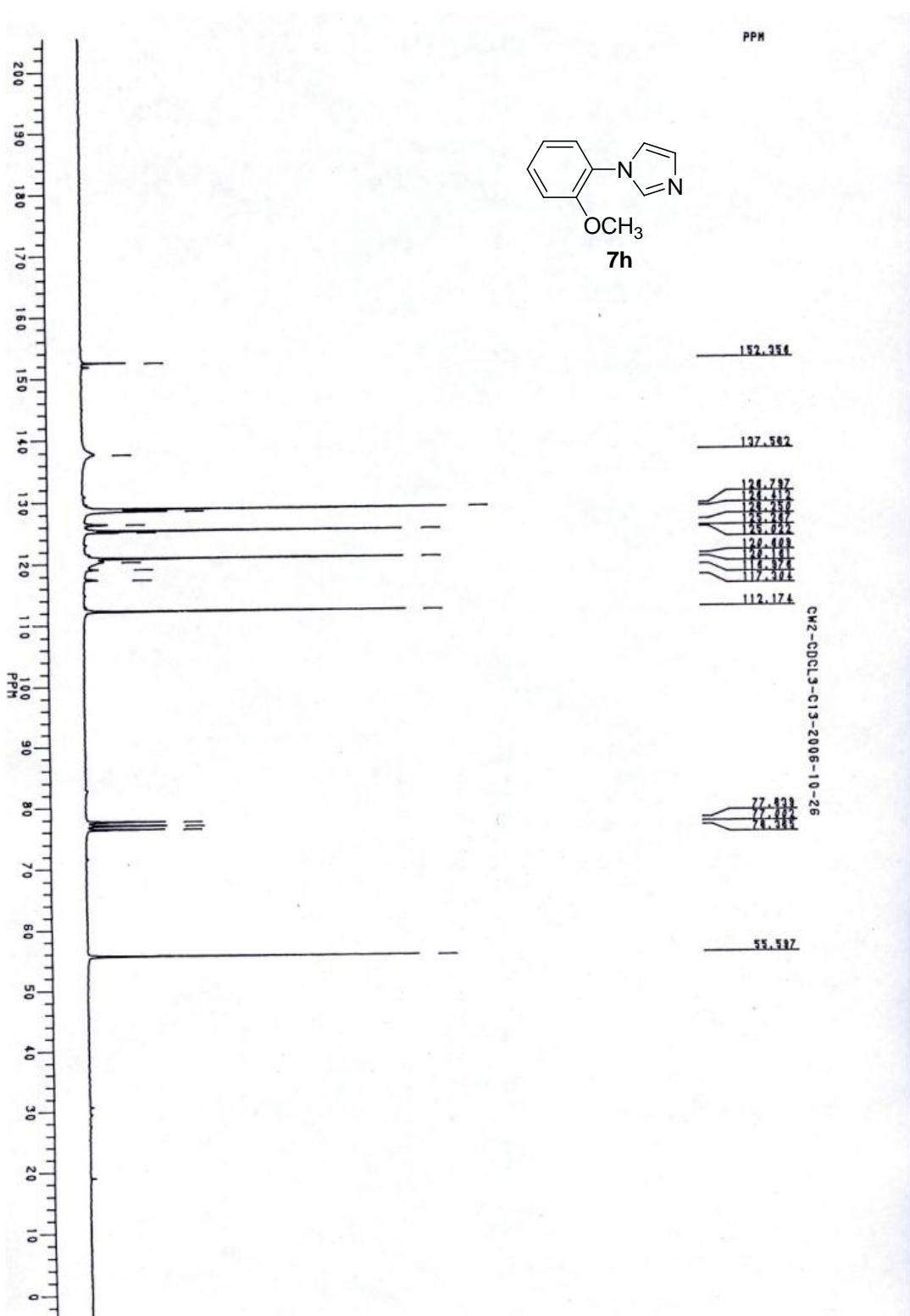
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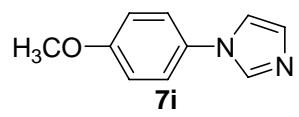
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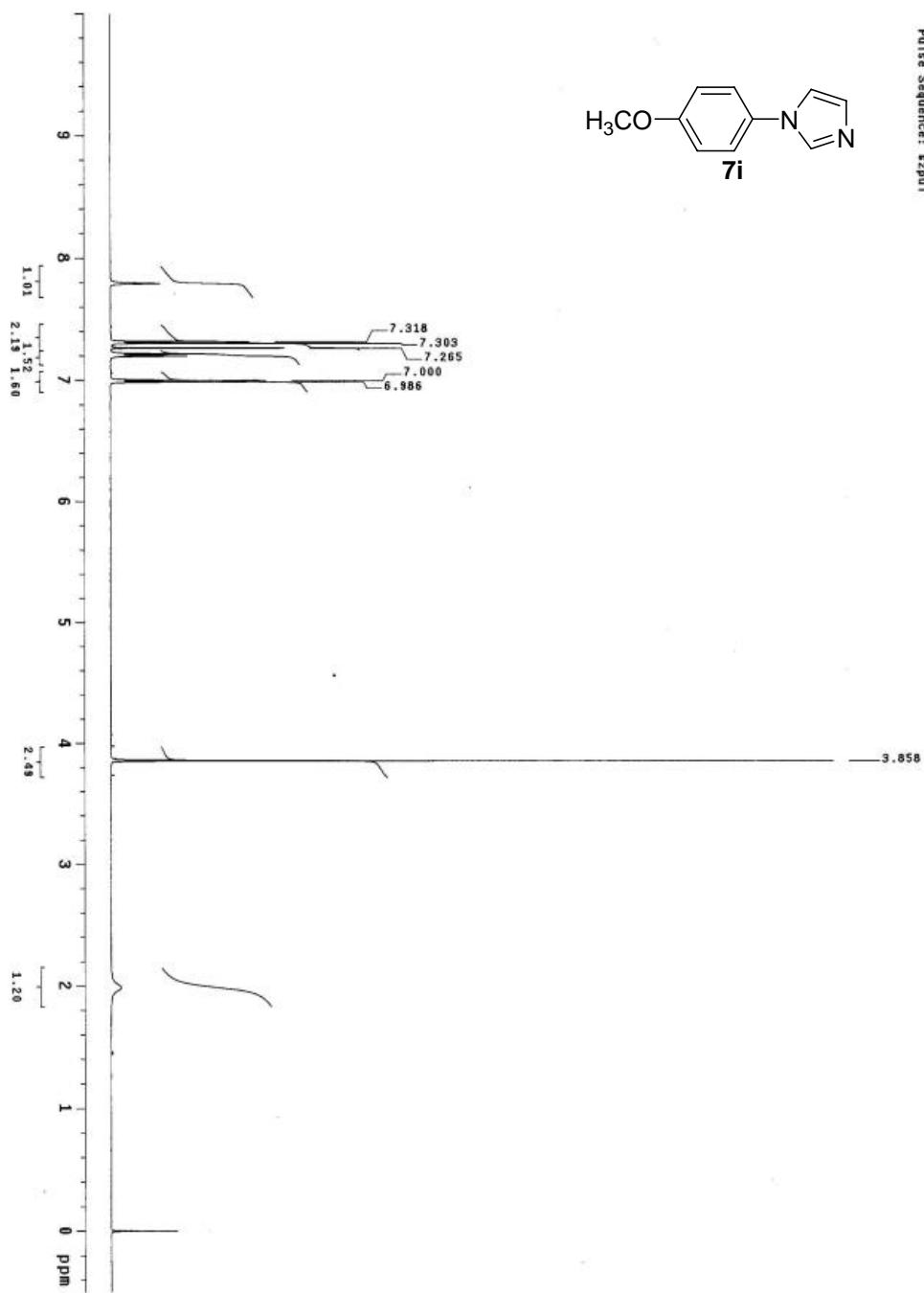
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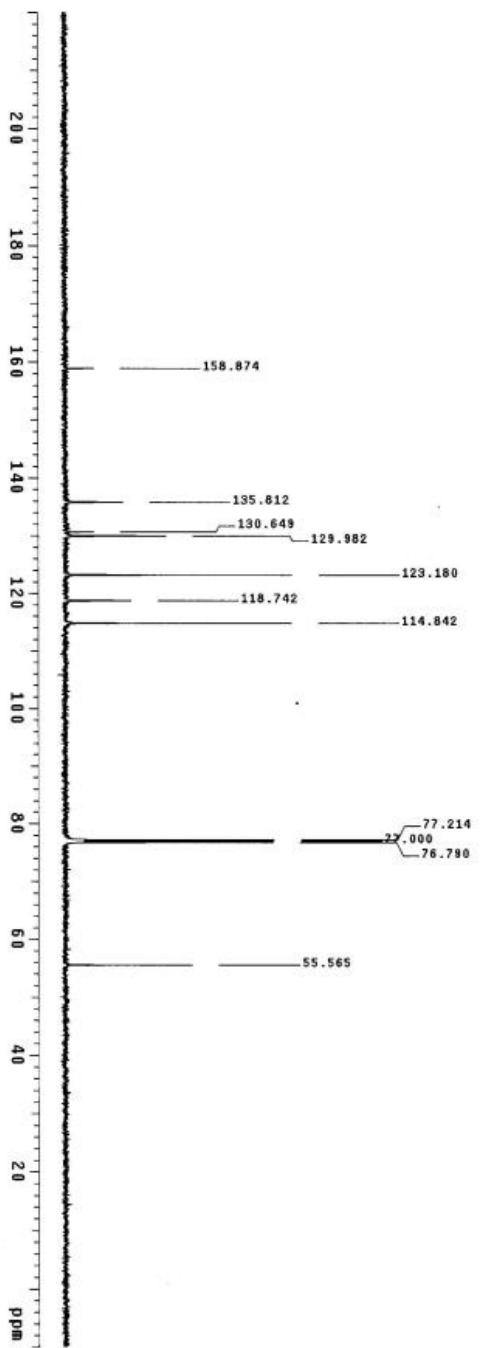
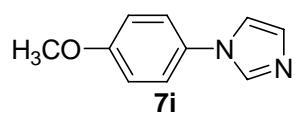


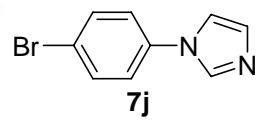


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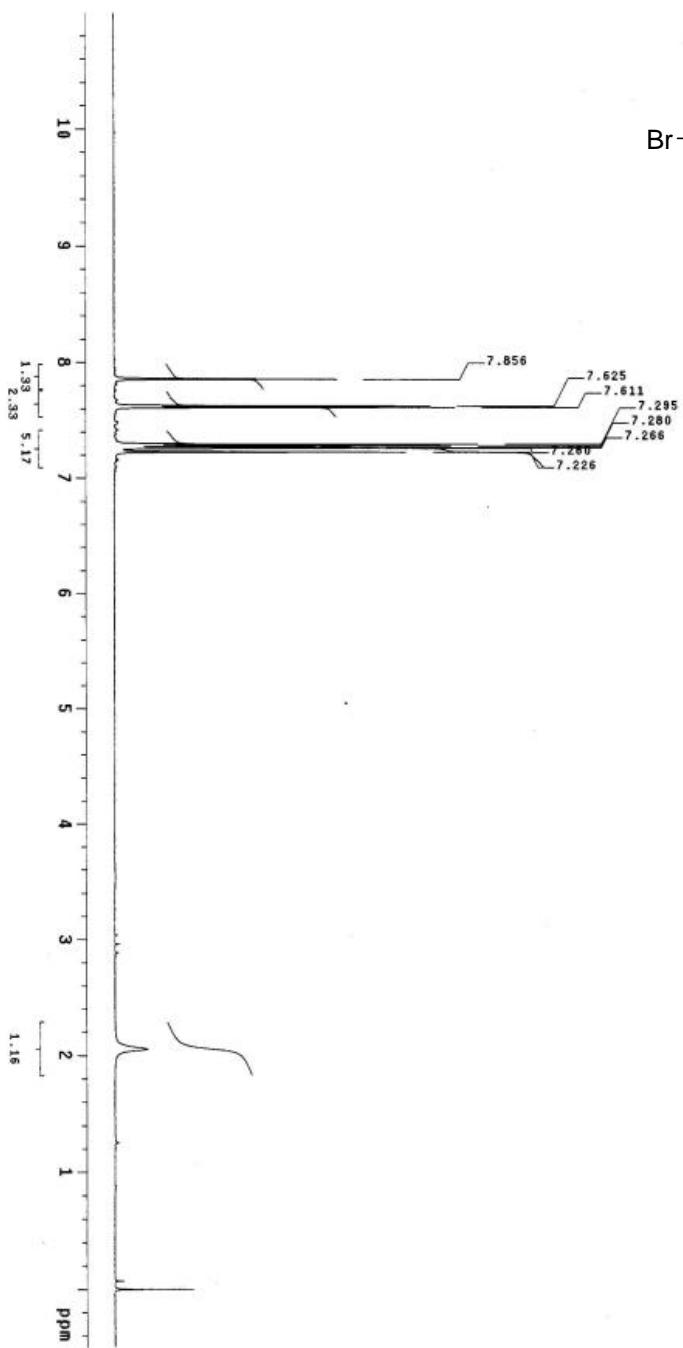


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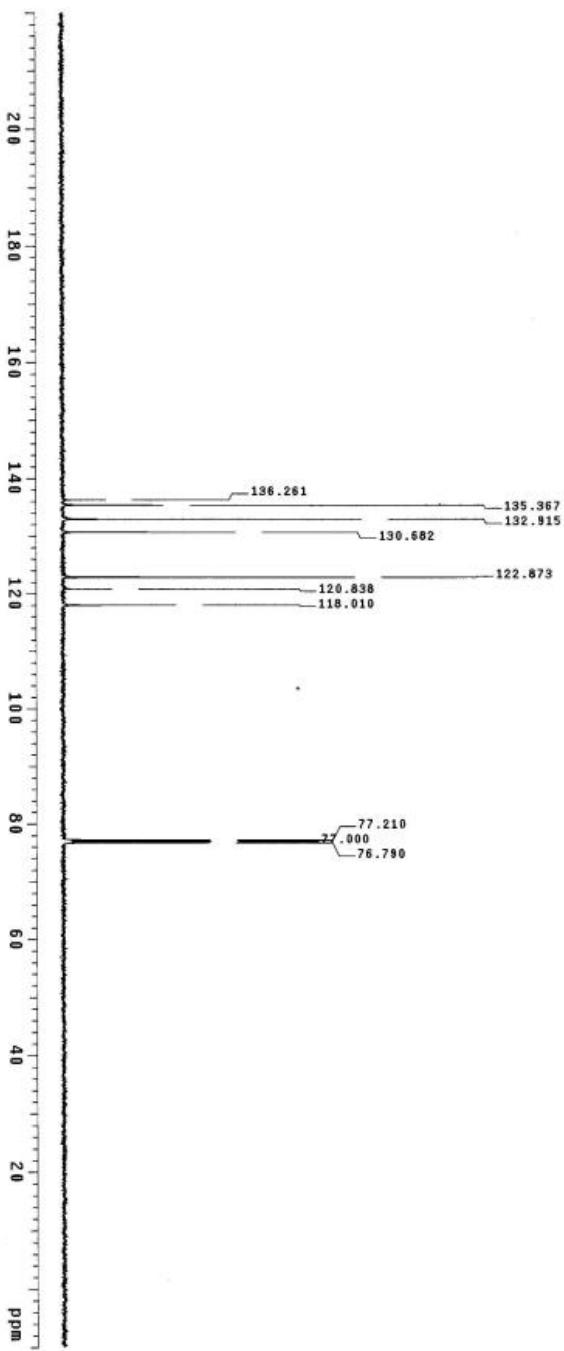
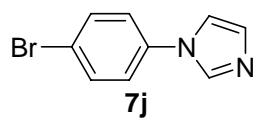


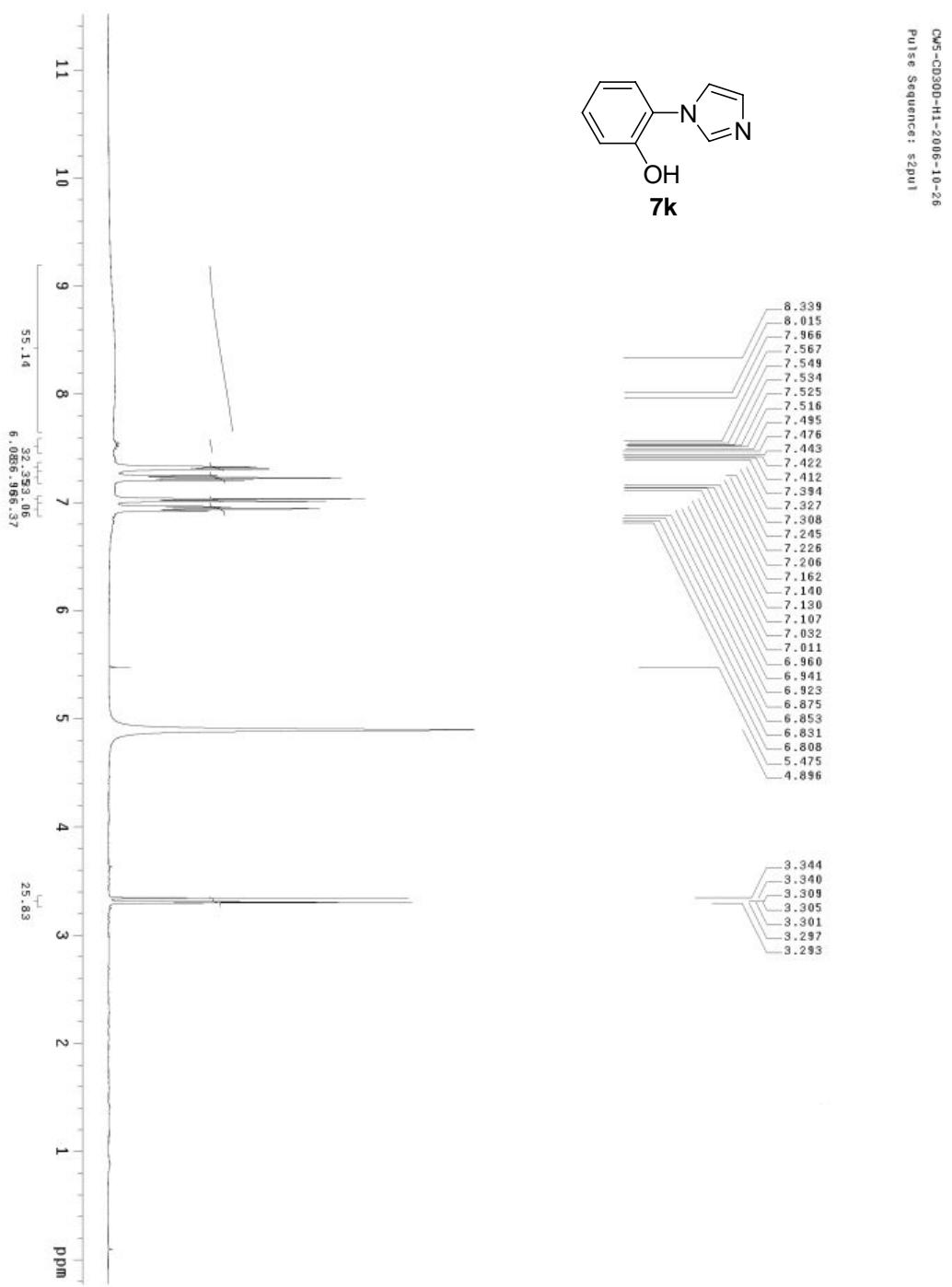


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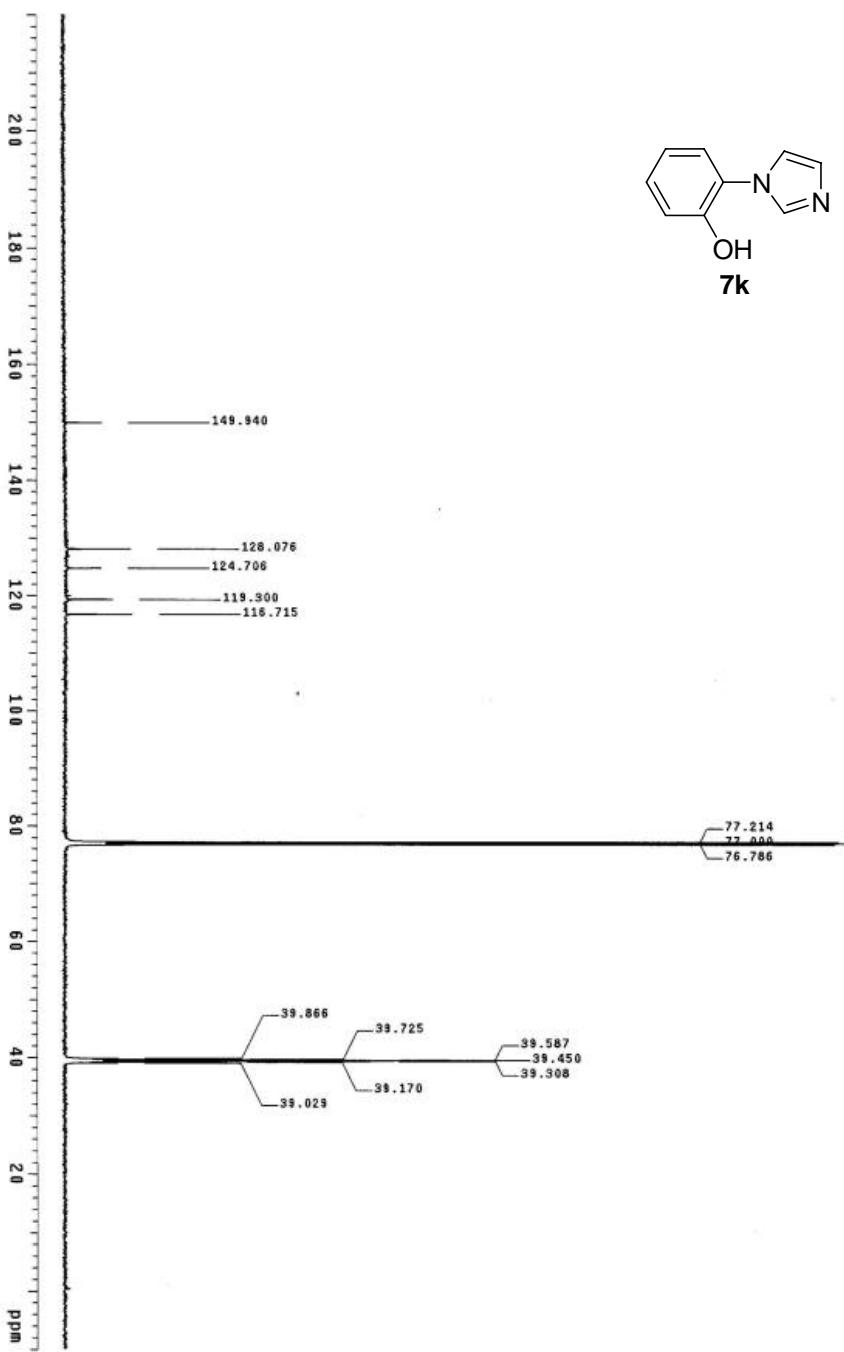
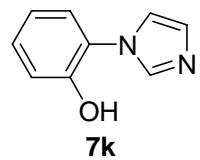


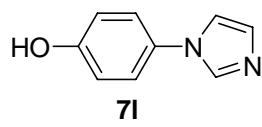
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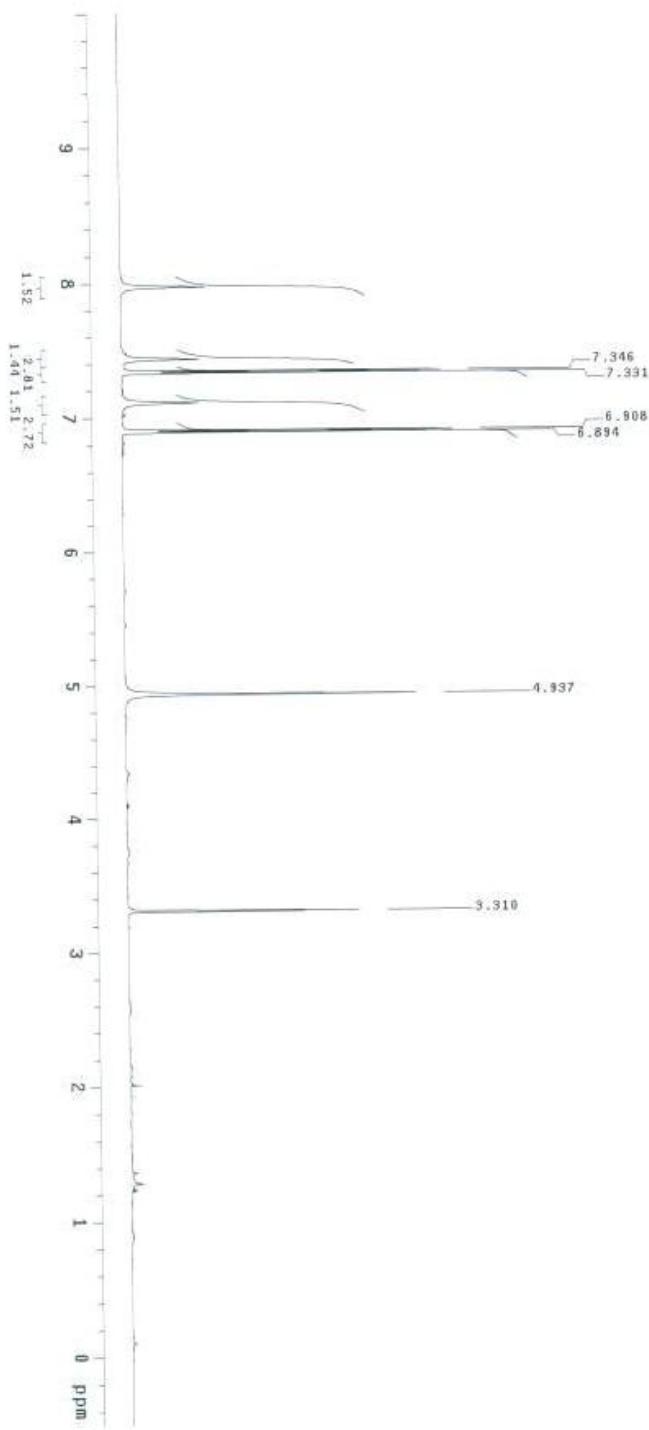


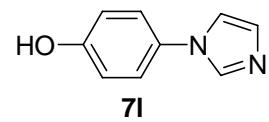
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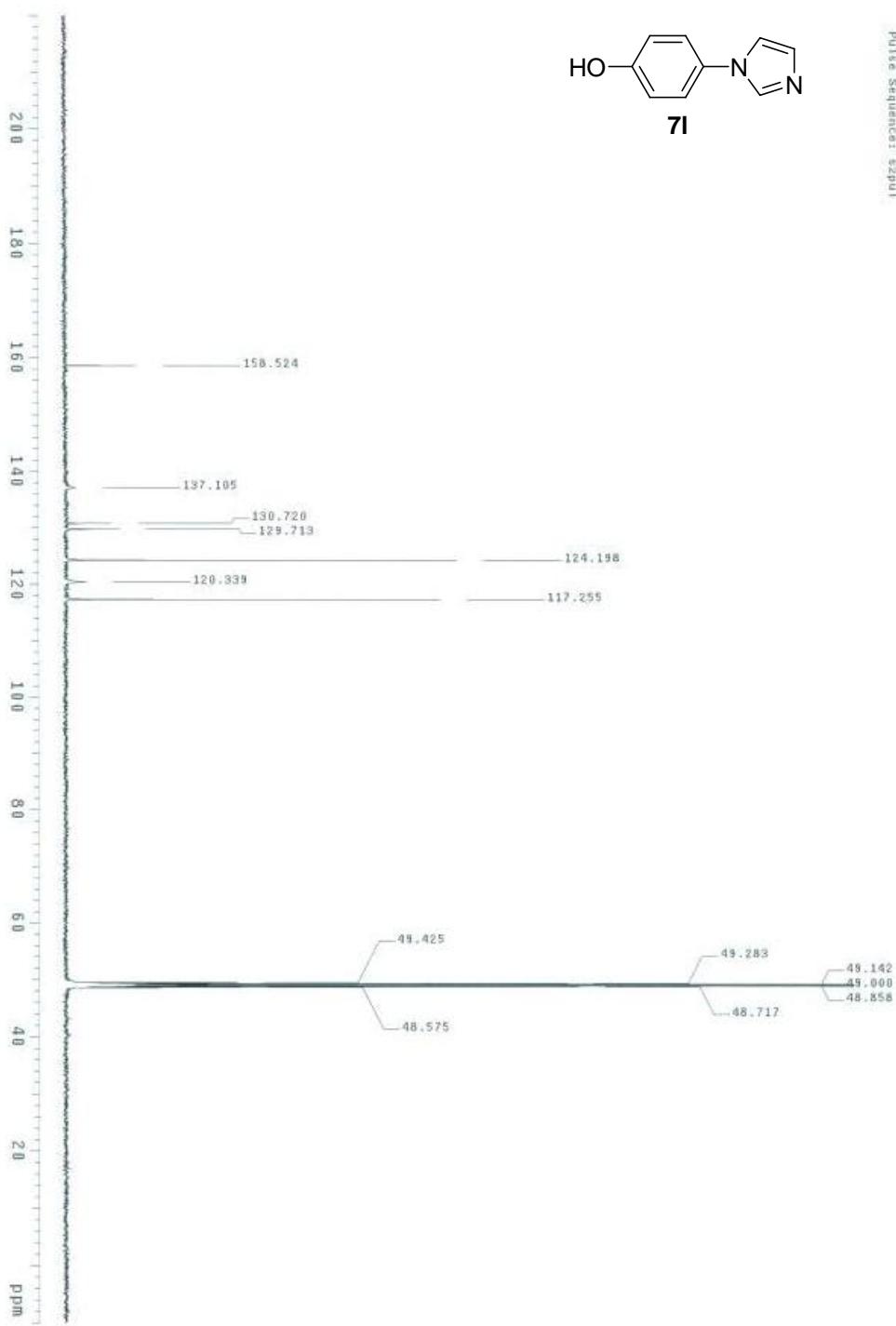


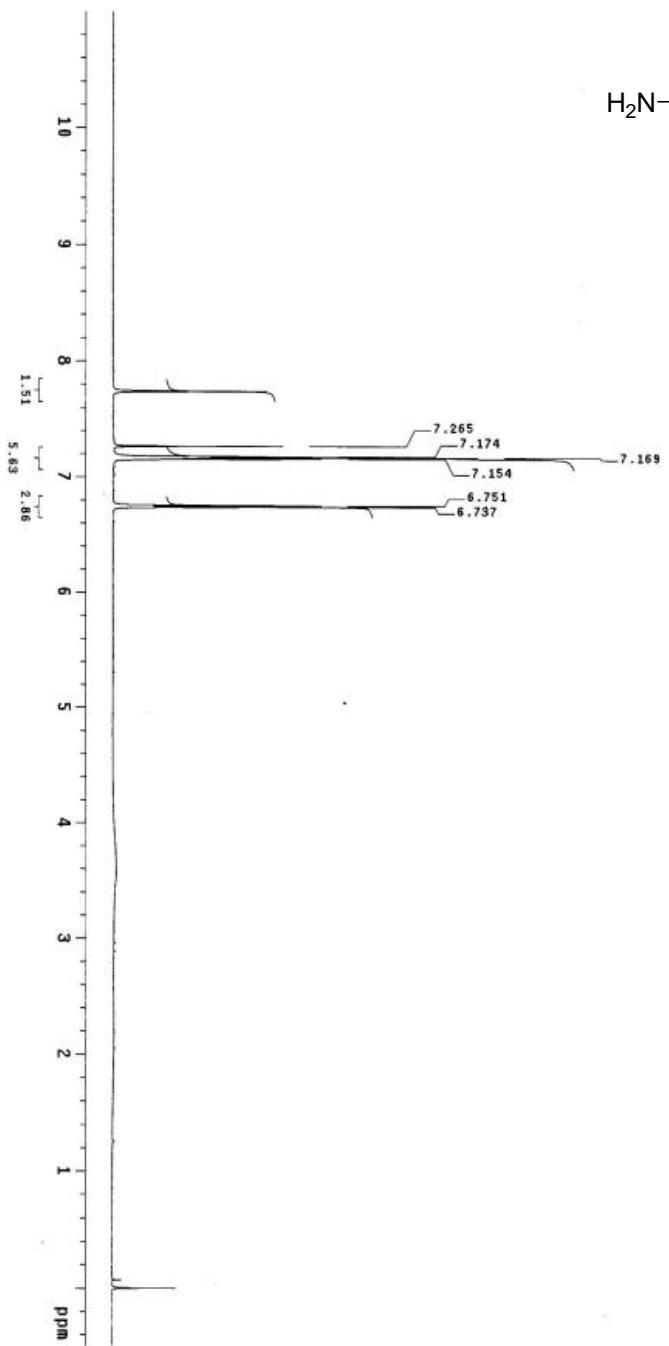
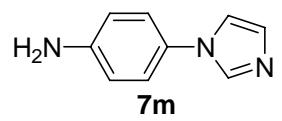
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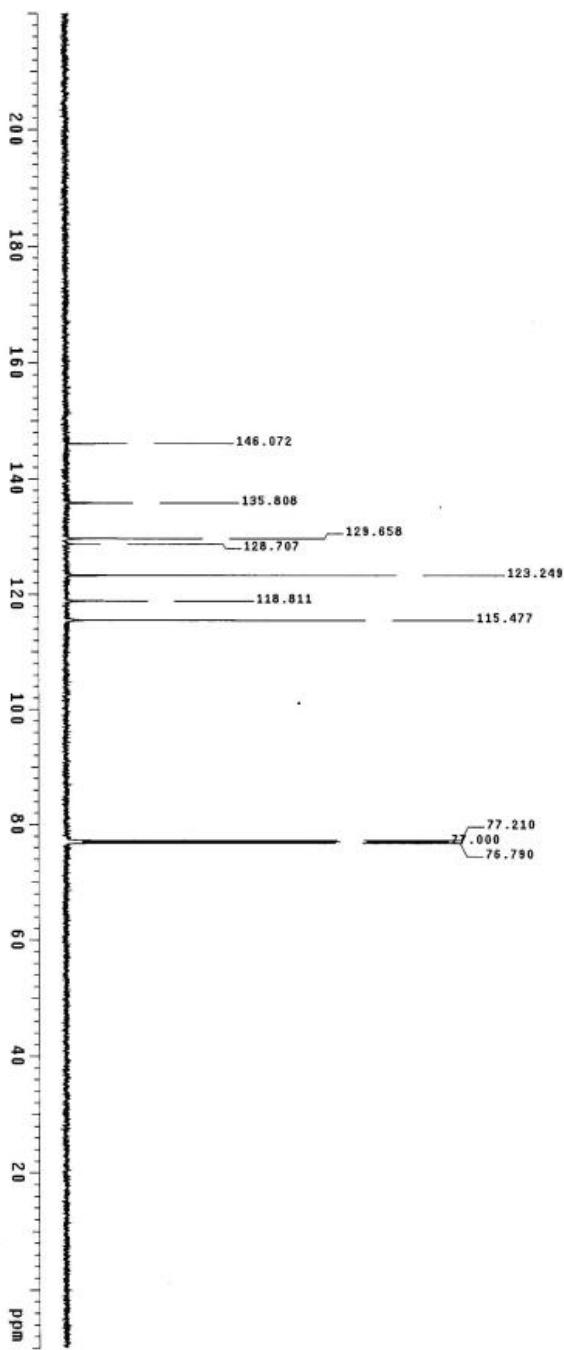
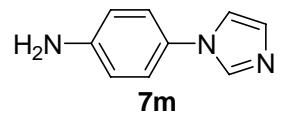


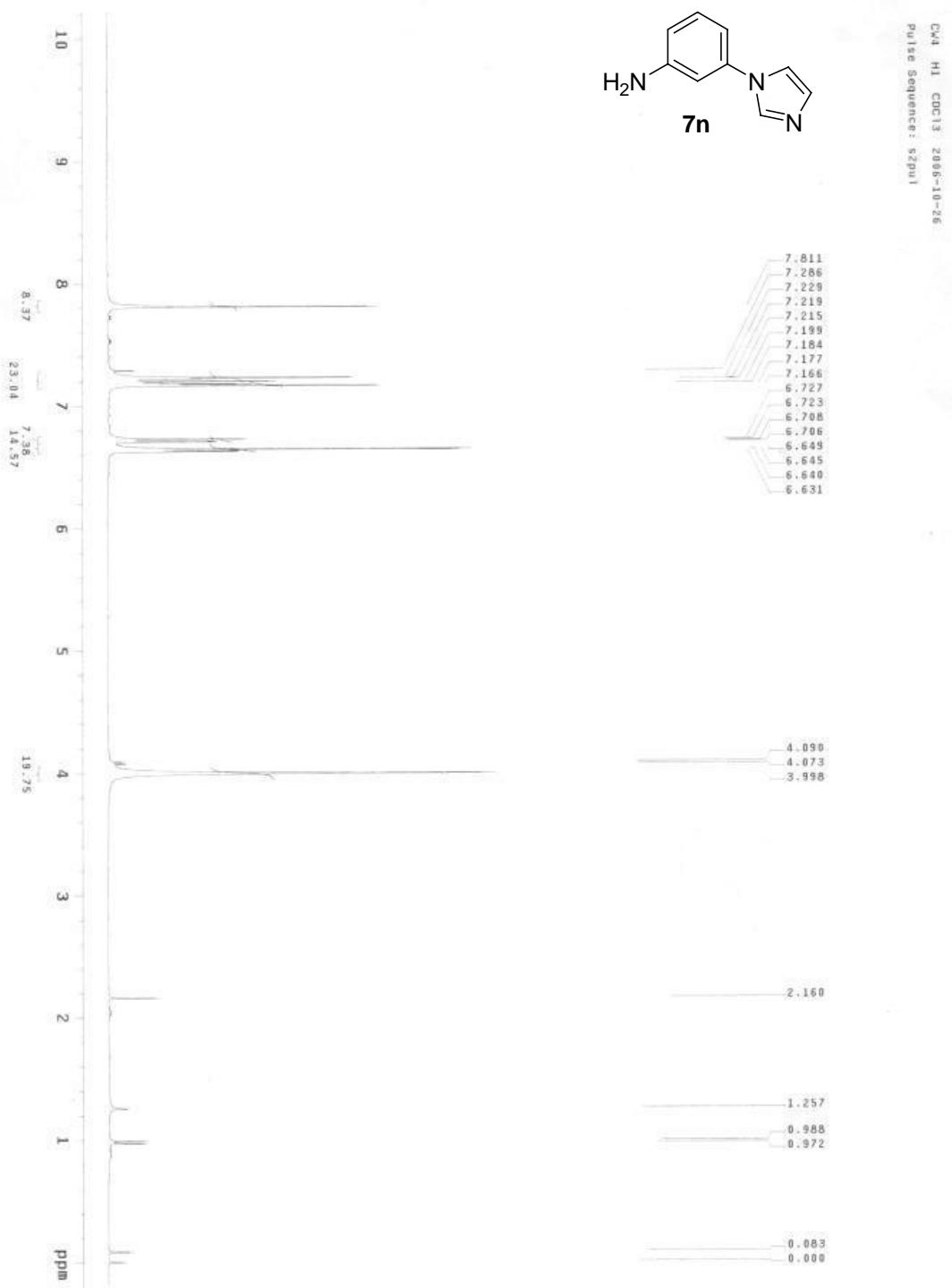


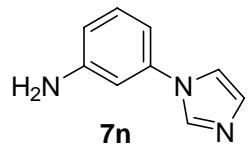
Y4S-0817=7
Pulse Sequence: 82μT



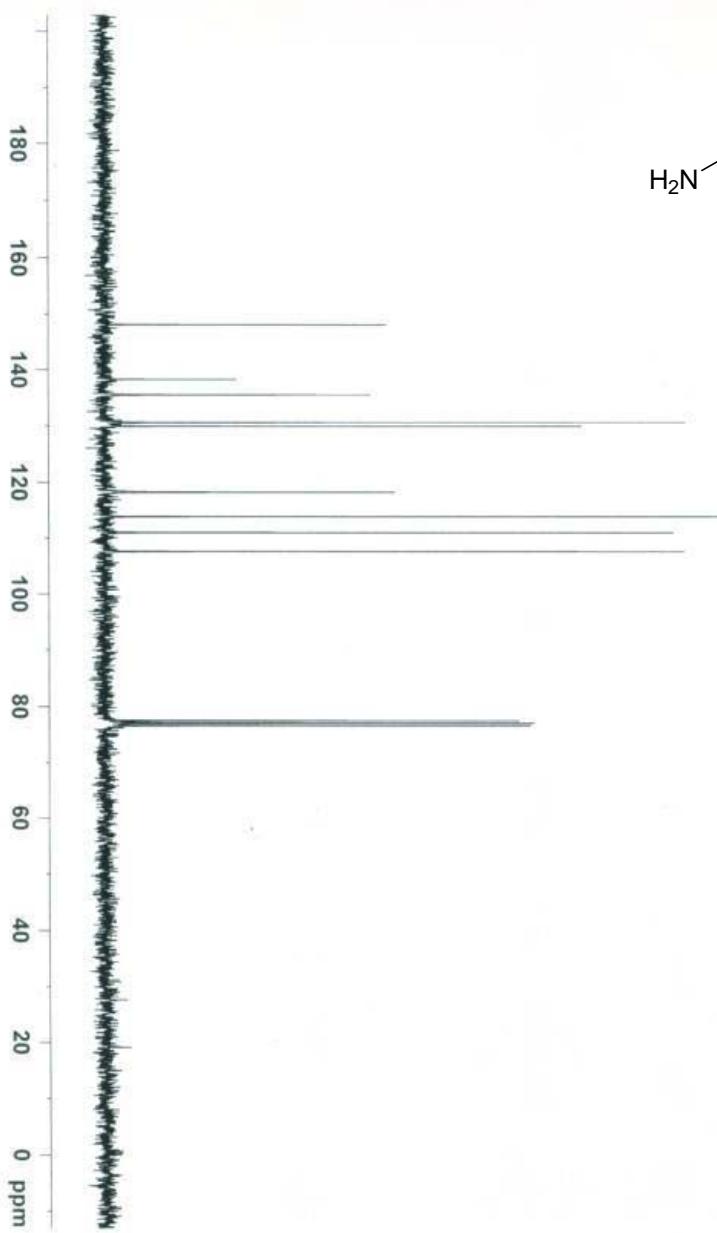








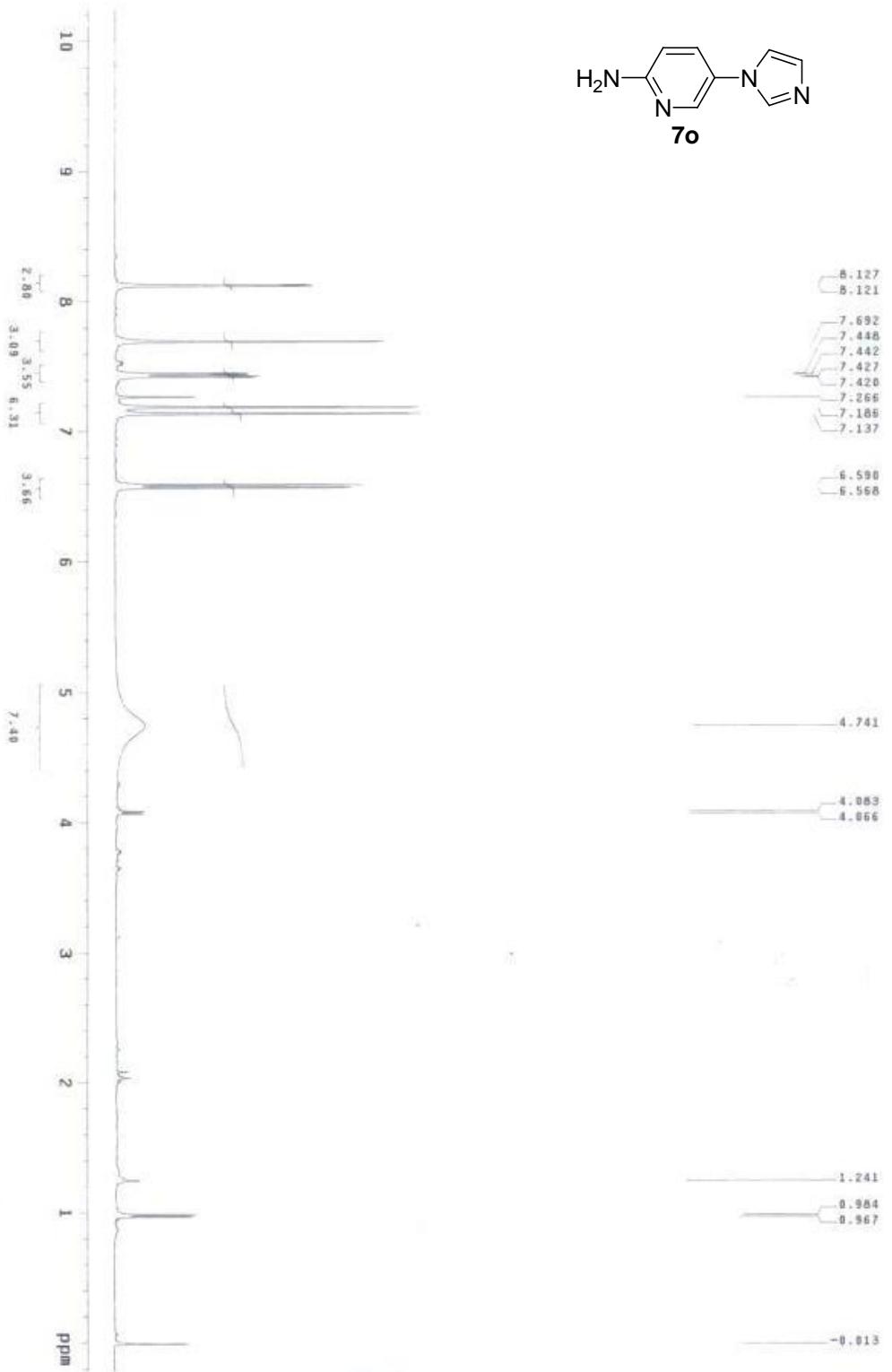
149.1181
 138.3260
 135.5914
 130.6331
 129.9987
 118.2823
 113.9096
 111.0510
 107.6562
 77.5705
 77.1462
 76.7225

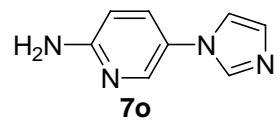


Current Data Parameters
 NAME C6H4_13C
 EXPT 1
 PROGNO 1
 F2: - Acquisition Parameters
 Date 20061026
 Time 15:14
 INSTRUM av300
 PROBHD 5 mm PABBO BB-
 PULPROG zg3c30
 TD 5536
 SOLVENT CDCl₃
 NS 142
 DS 16
 SWH 18832.393 Hz
 FIDRES 0.287360 Hz
 AQ 1.7400308 sec
 RG 5100.6
 DW 26.550 usec
 DE 6.00 usec
 TE 298.4 K
 D1 1.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 6.00 usec
 F1 -6.00 dB
 SF01 75.4752960 MHz
 ===== CHANNEL f2 =====
 CPPRG2 1H
 NUC2 1H
 FCD2 80.00 usec
 PL1 45.00 dB
 PL2 16.00 dB
 SF02 300.131410 MHz
 F2 - Processing parameters
 SI 32768
 SF 75.4677490 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40







4-1-2802-615-1702-1902
1528 : 3400-3000, 3150-2800
1428-234

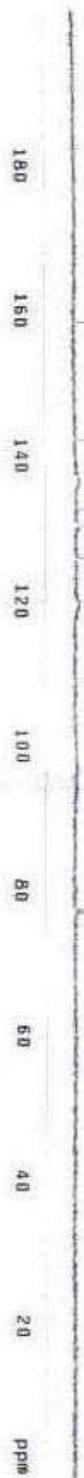
142, 979

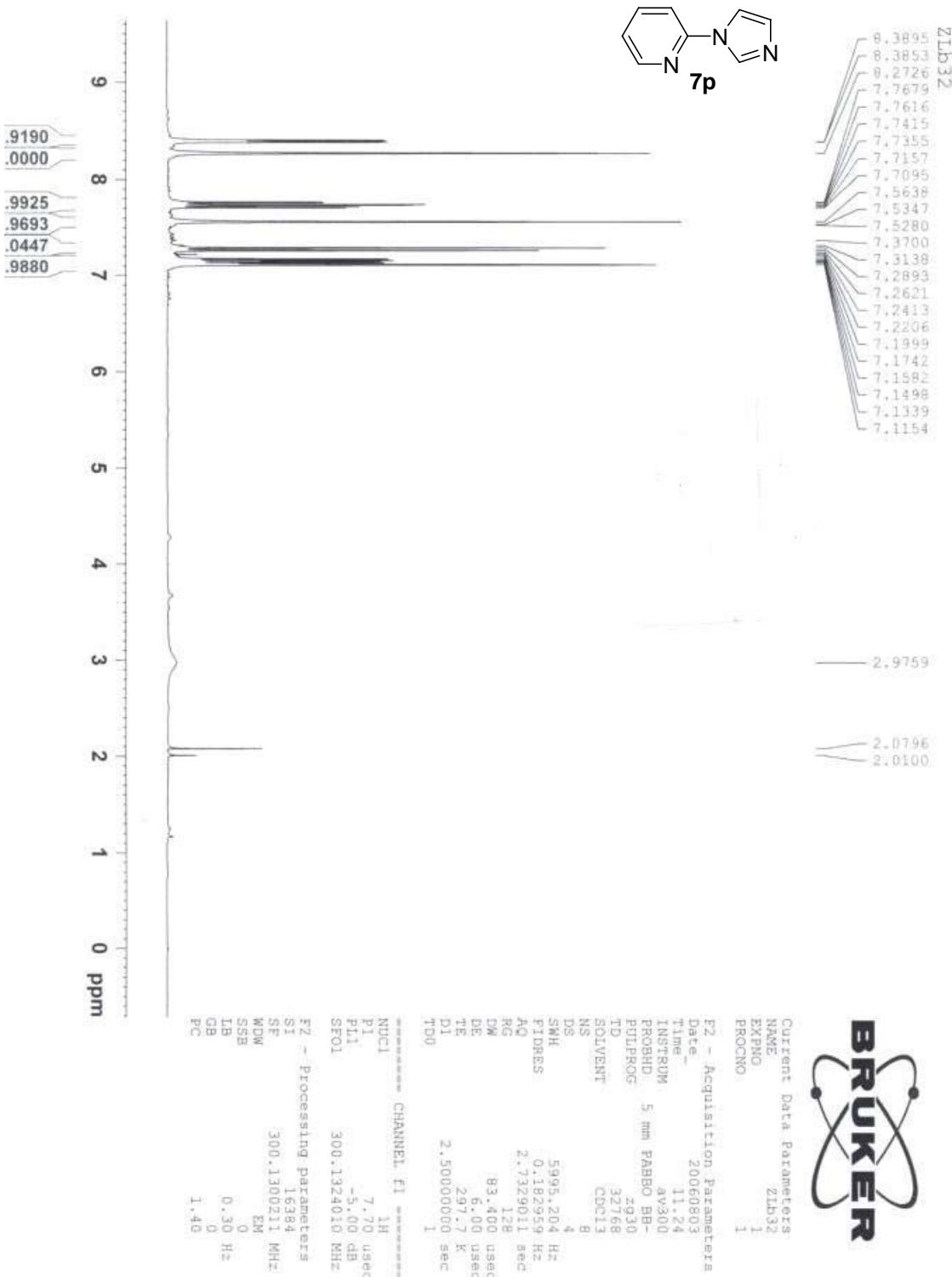
137, 511
130, 263

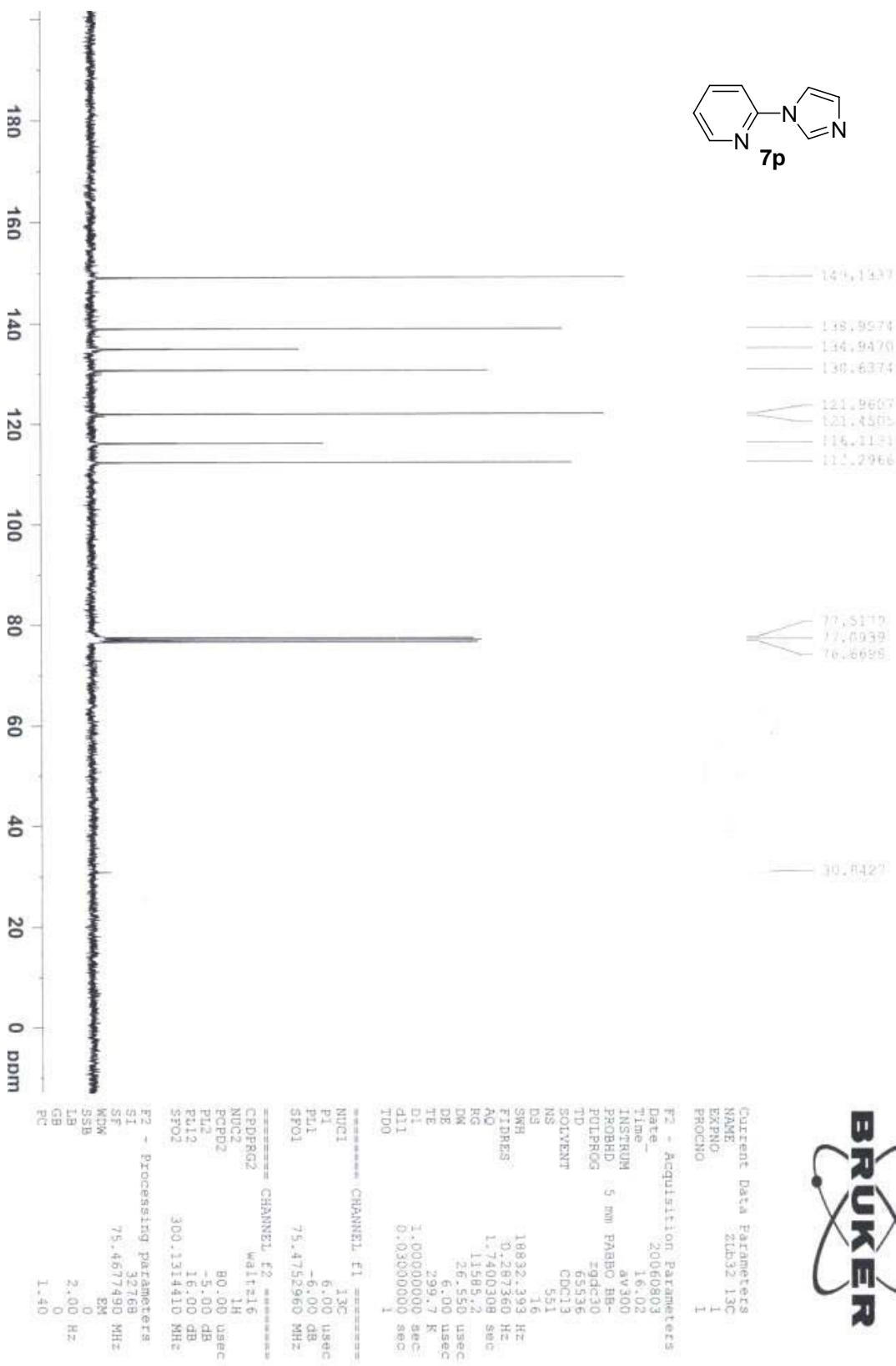
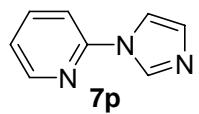
125, 734

108, 711

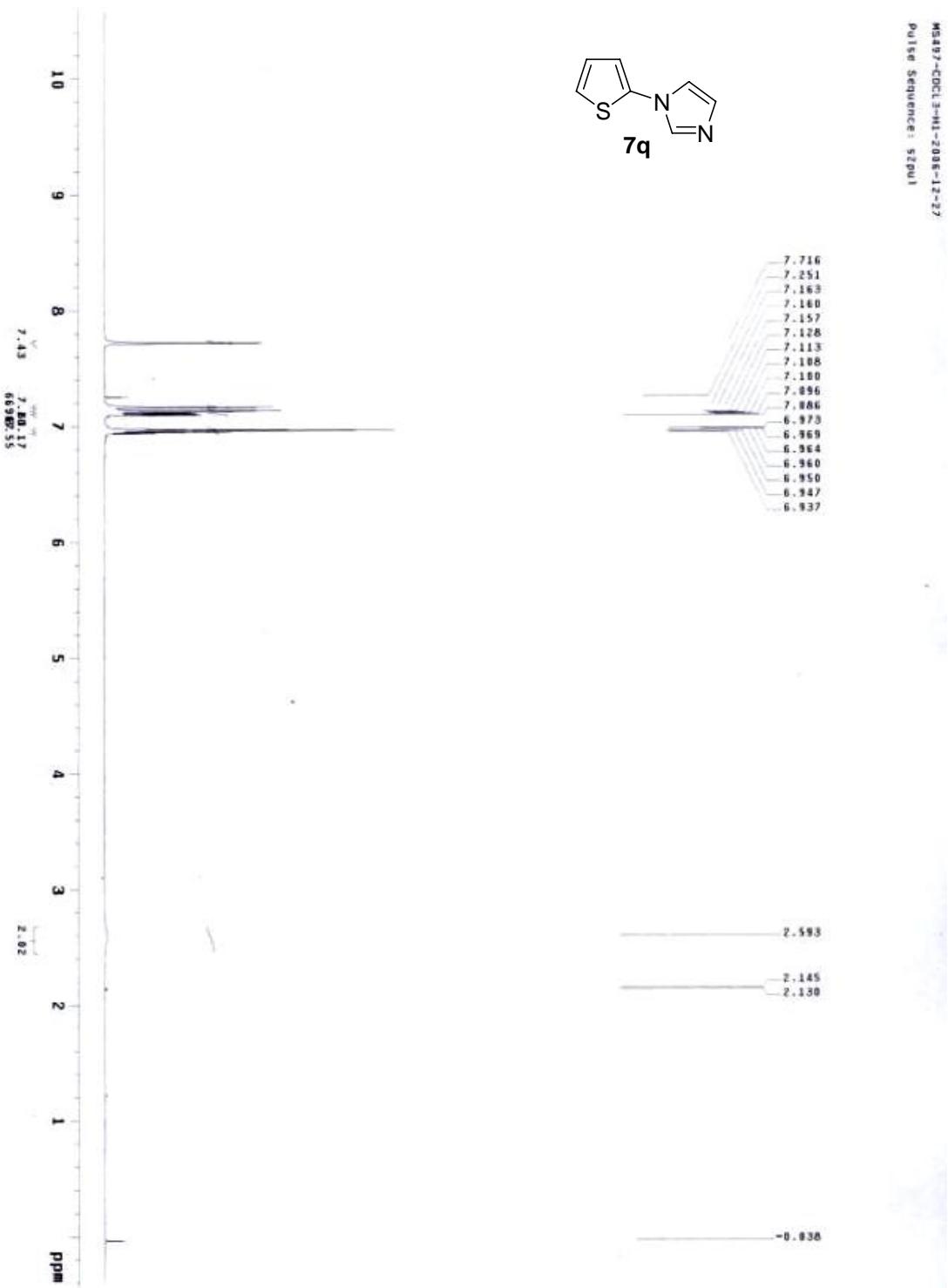
77, 487
77, 176
76, 895



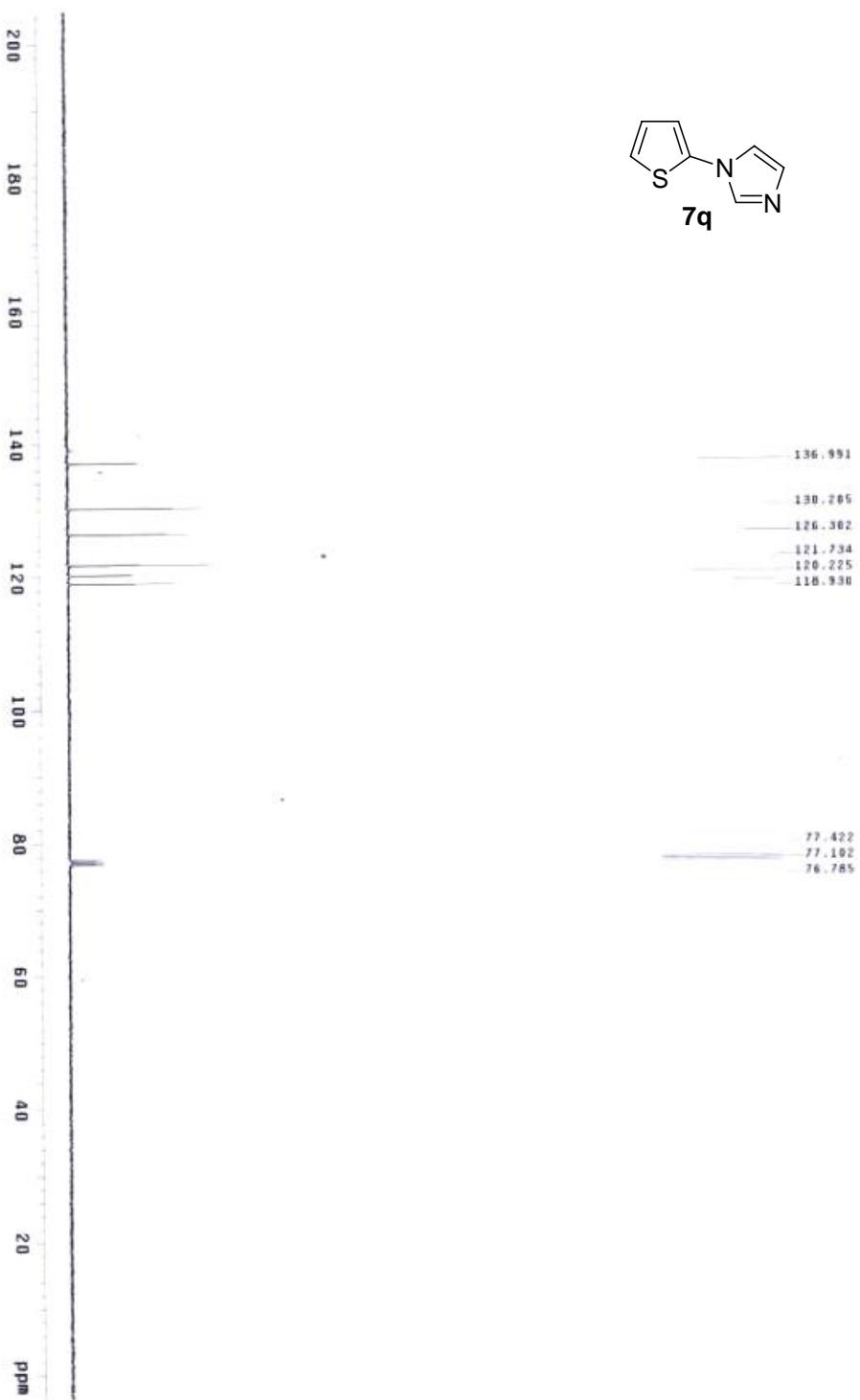
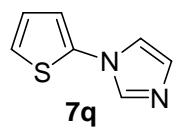


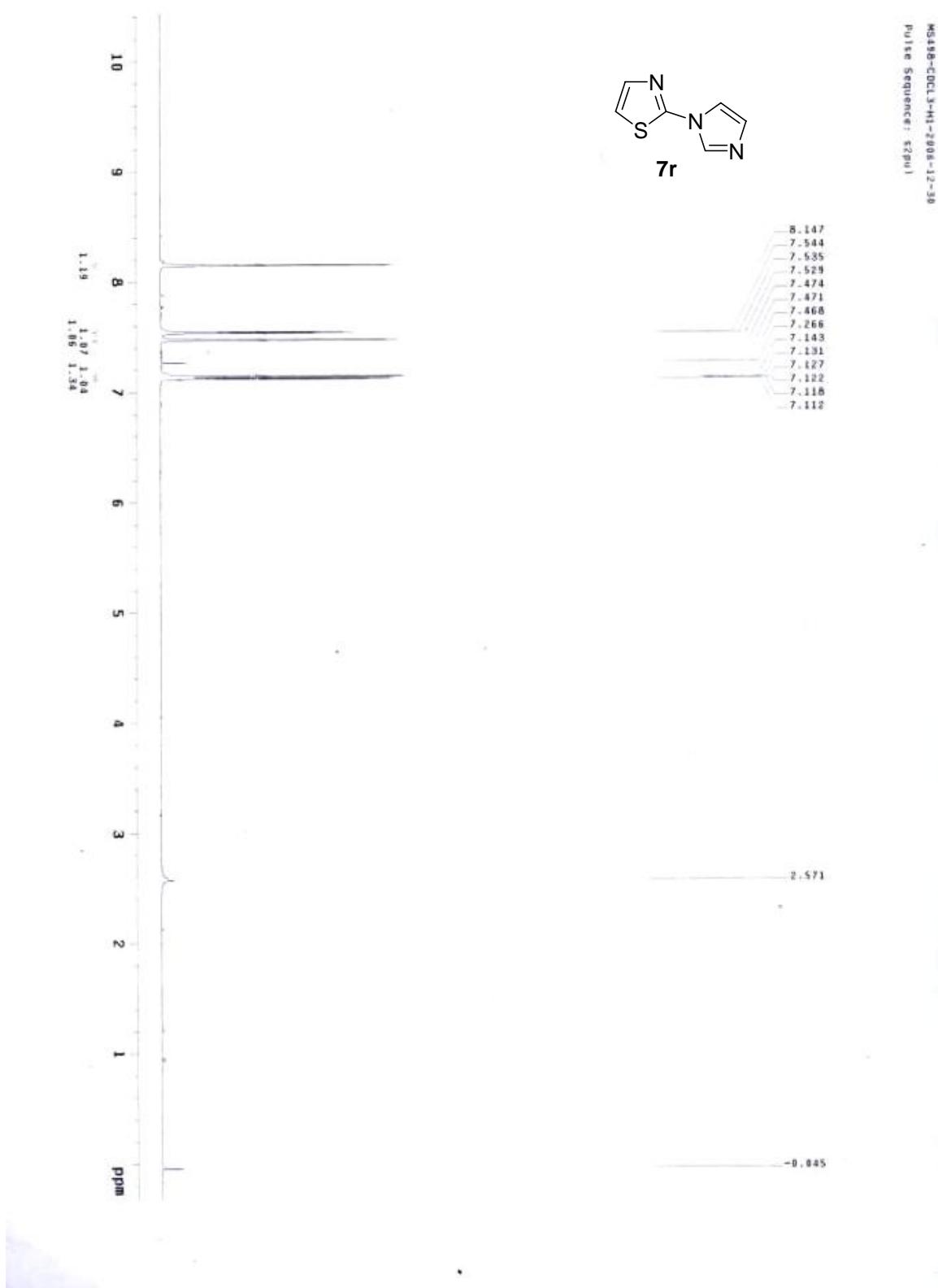


BRUKER

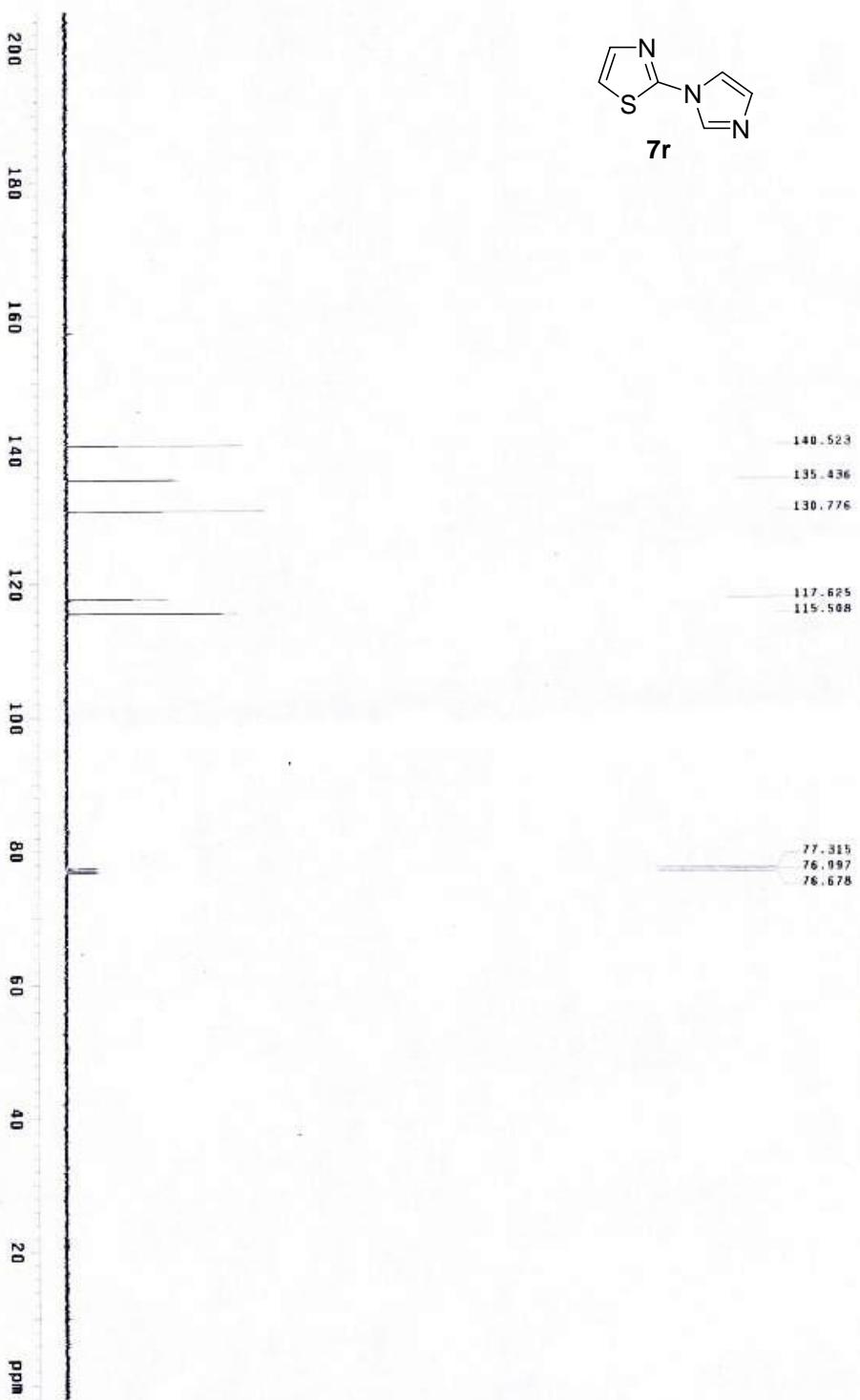
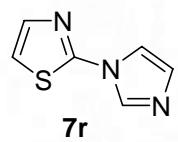


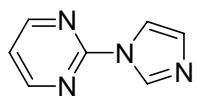
MS4.9 -CDCl₃-C₆H₆-2006-12-31
pulse Sequence: 82mu1



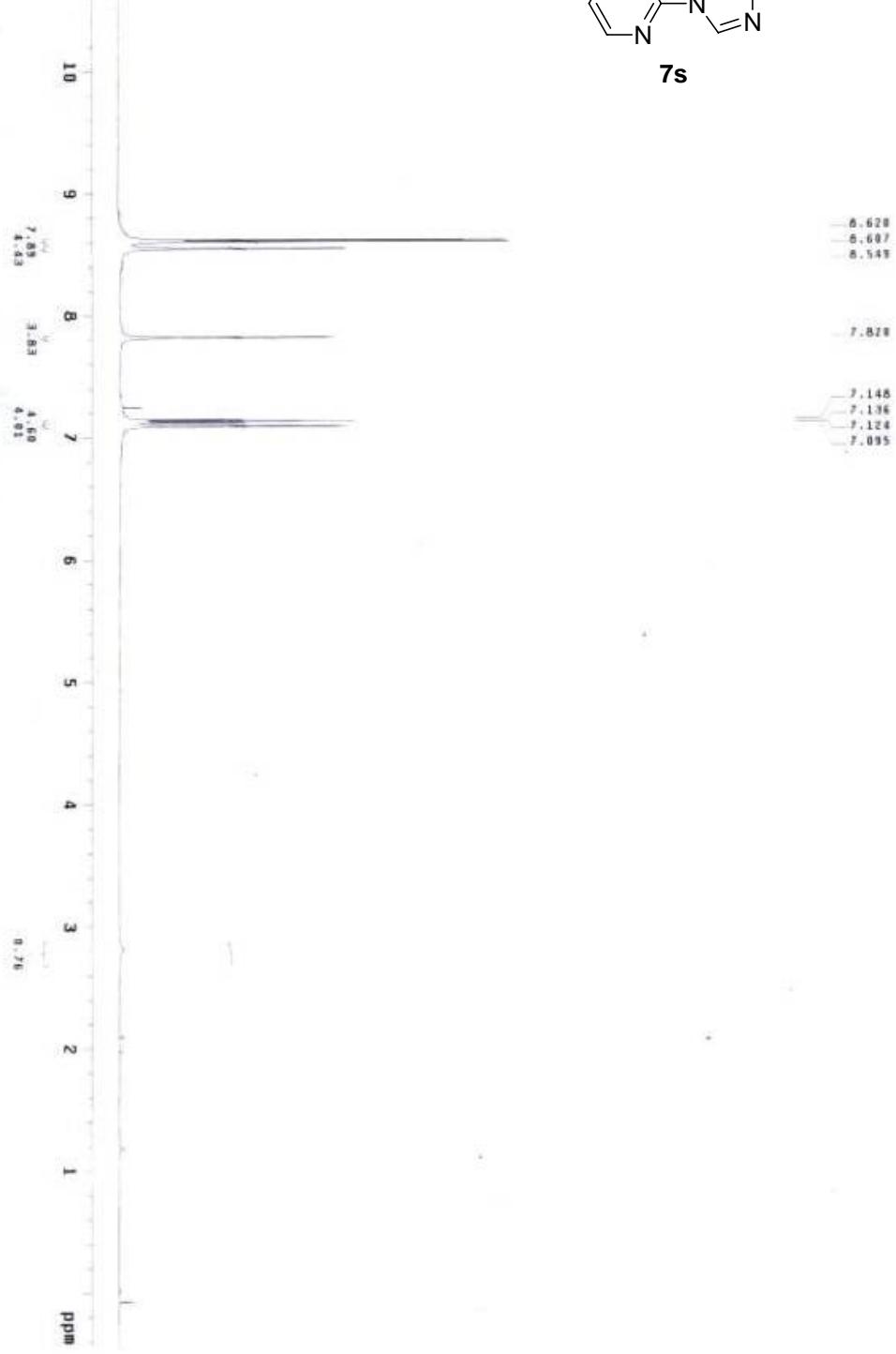


MS498-CDCl₃-Cl₃-2007-1-4
Pulse Sequence: S2P1

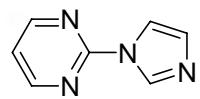




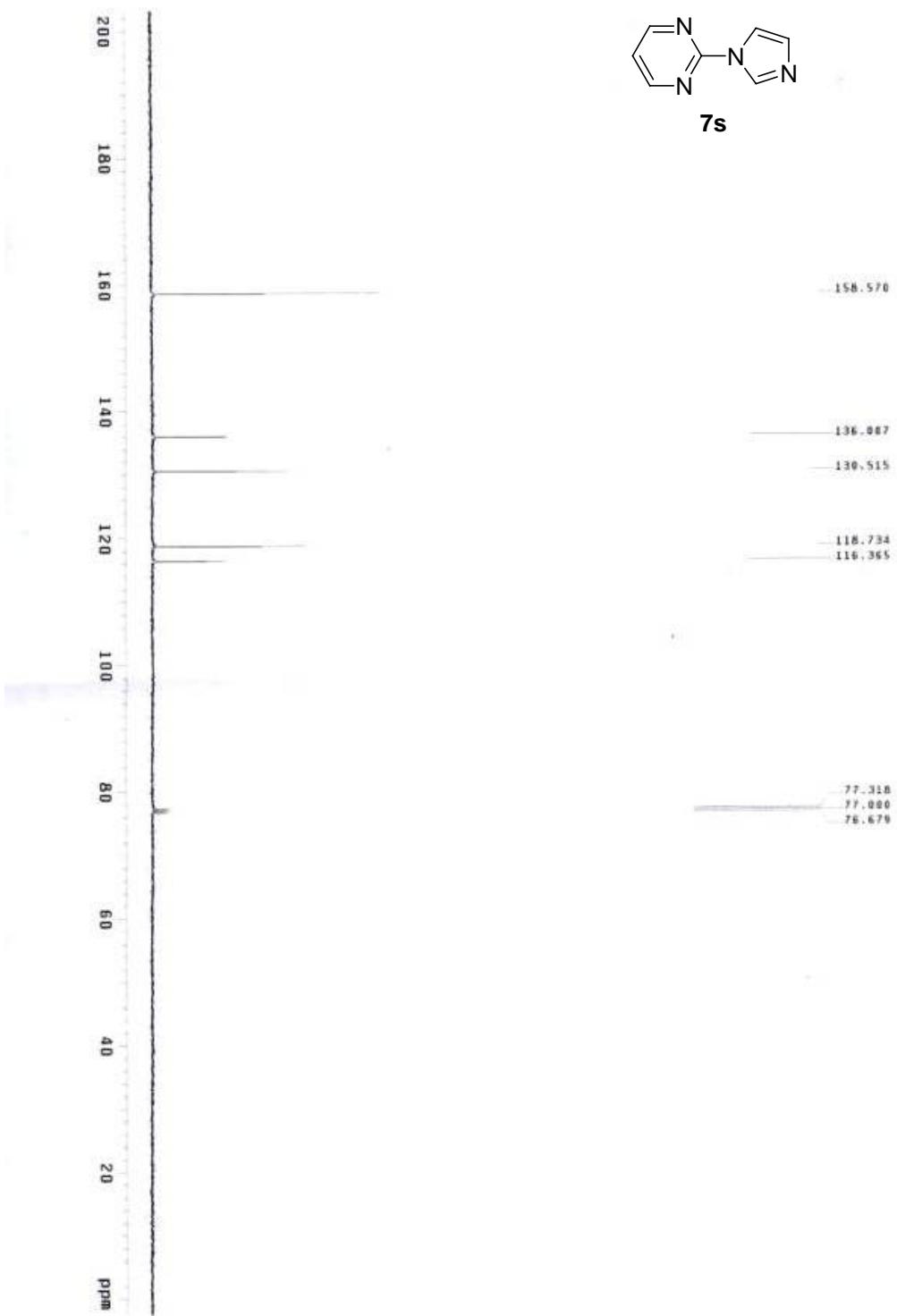
7s

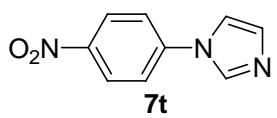


MS444-CDCl₃-C13-2886-12-30
Bruker Sequence: 52001

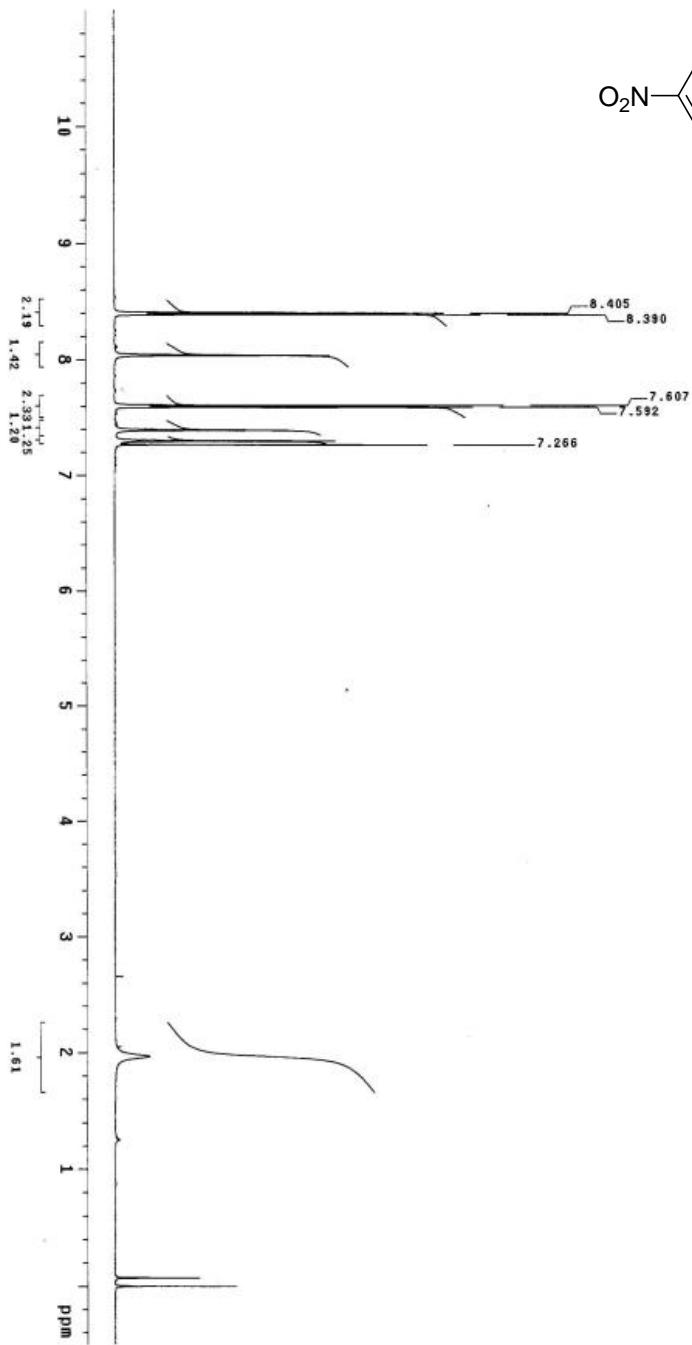


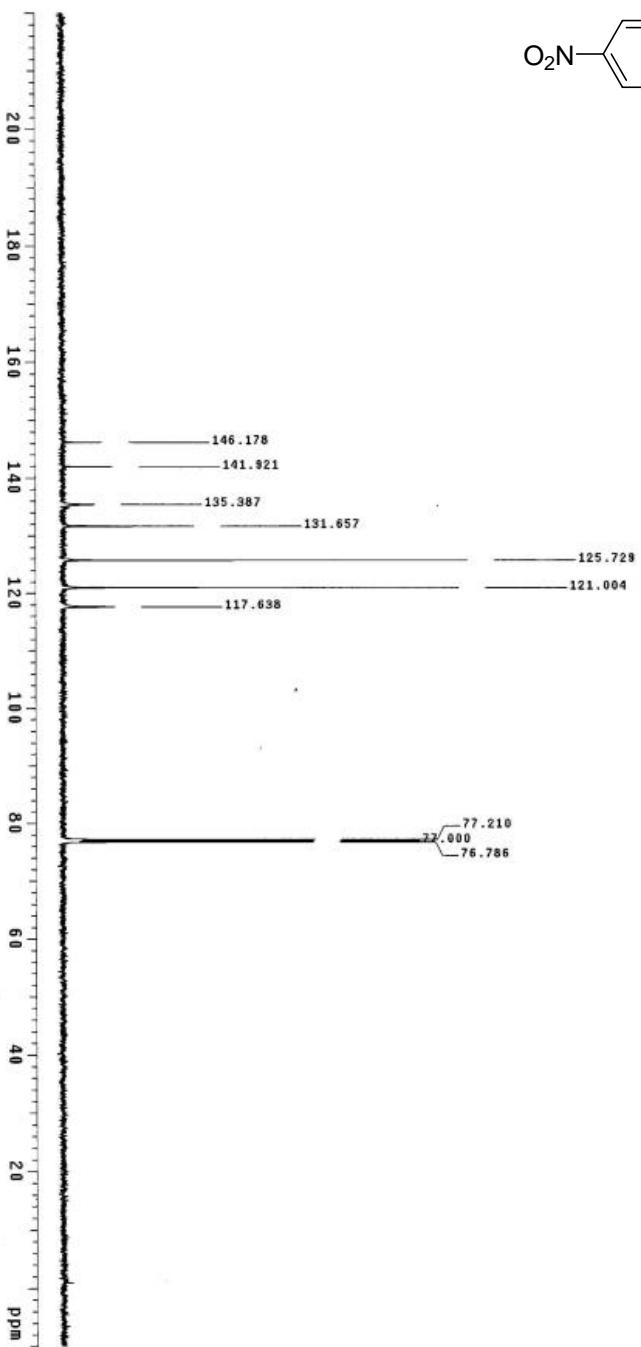
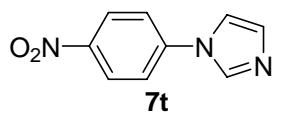
7s

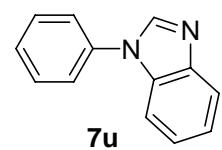




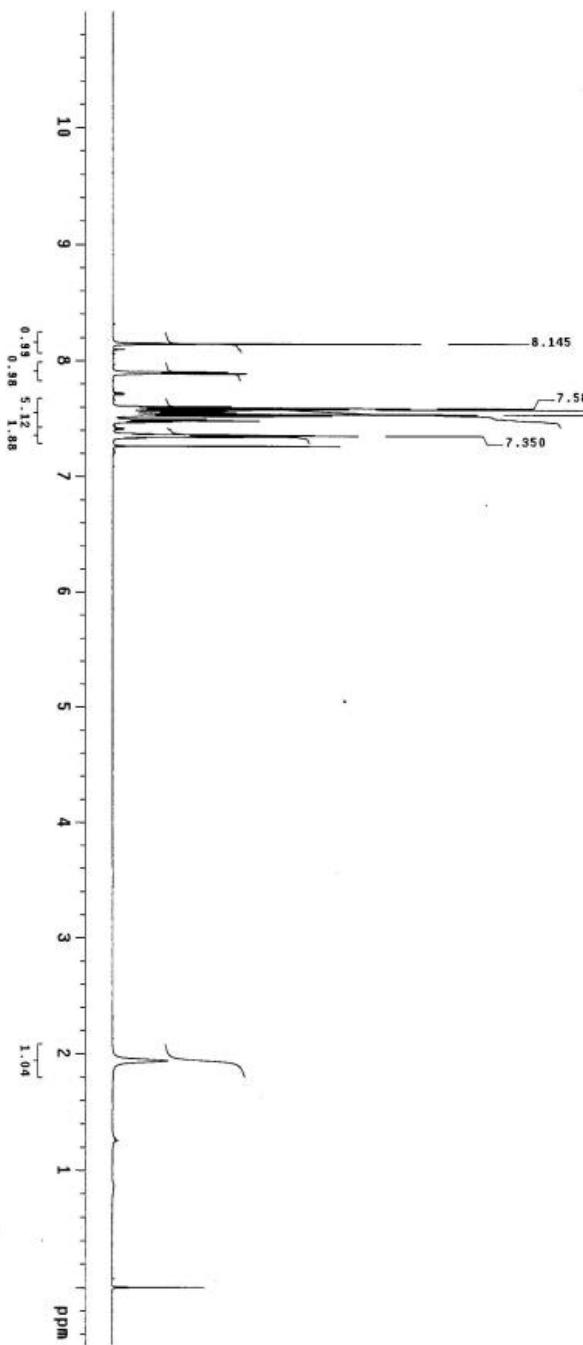
YJS-6000-18
Pulse Sequence: s2pul



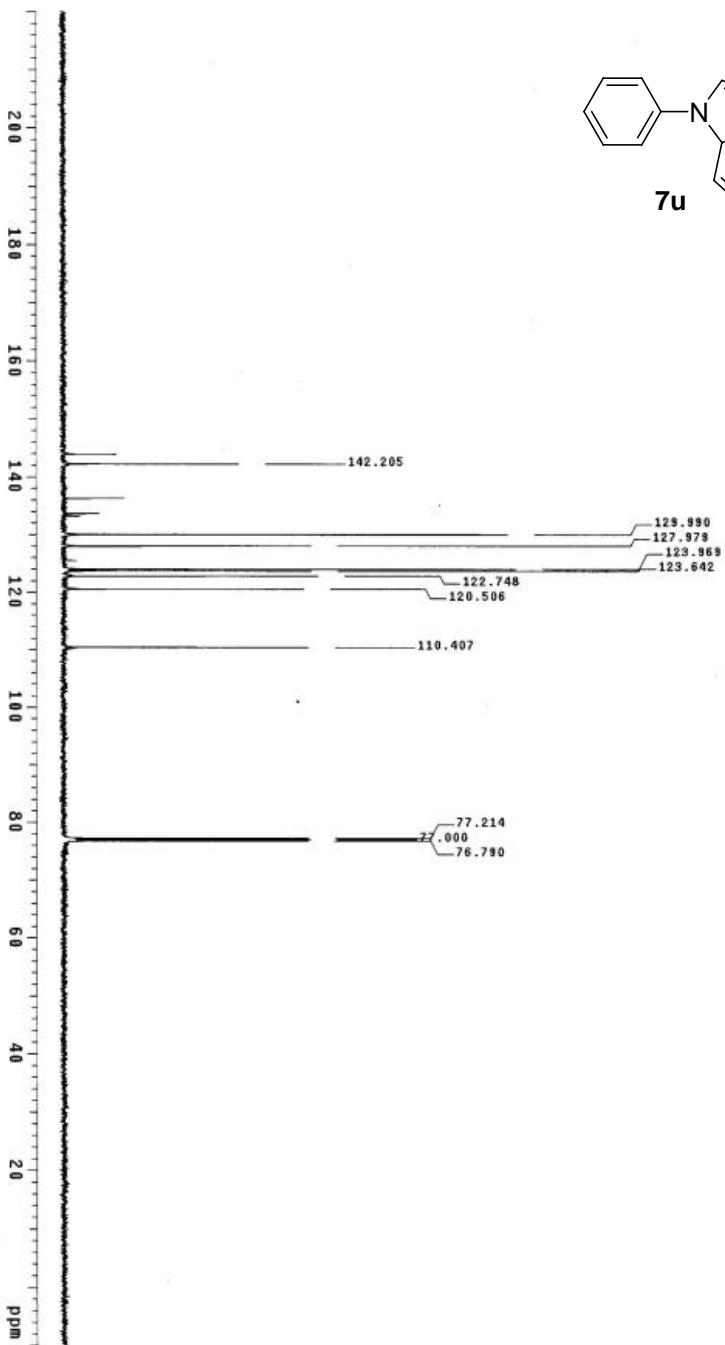
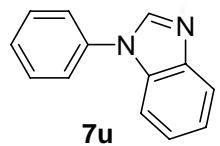




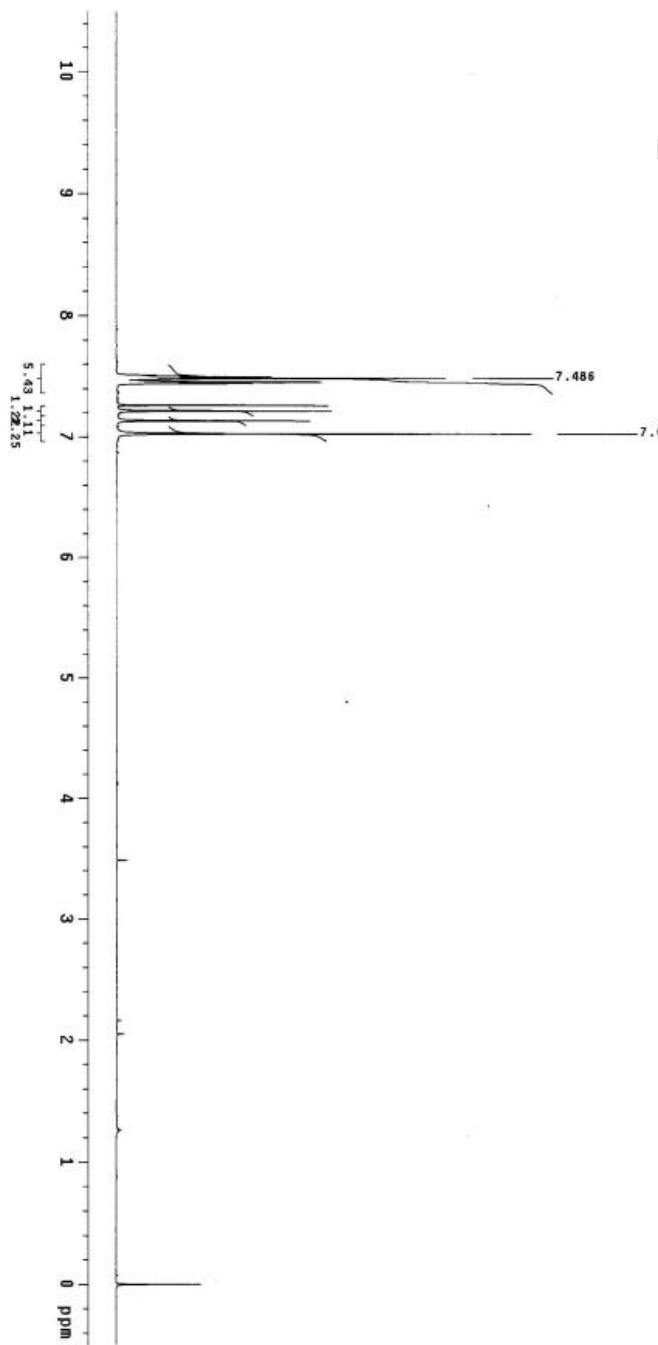
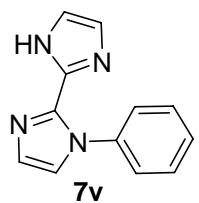
VJS-0906-13
Pulse Sequence: 62pu1



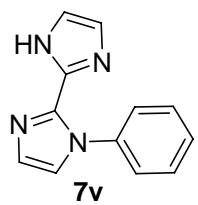
YJS-0606-13
Pulse Sequence: s2pul



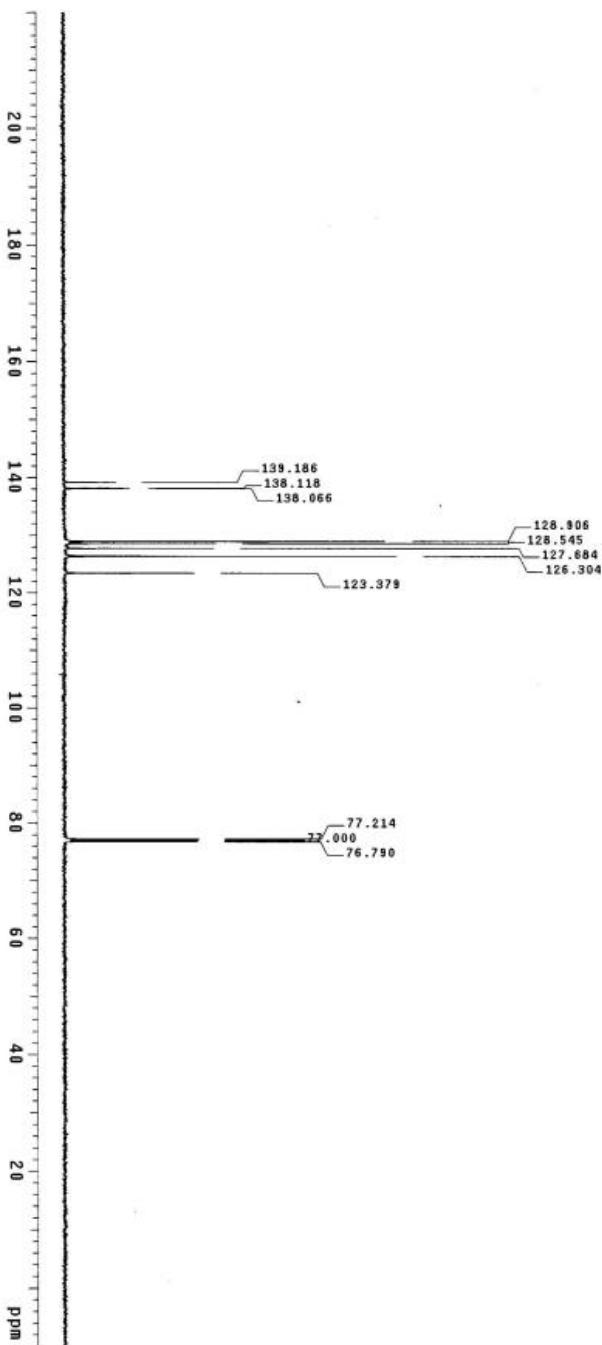
YJS-0005-9
Pulse Sequence: 62pu1

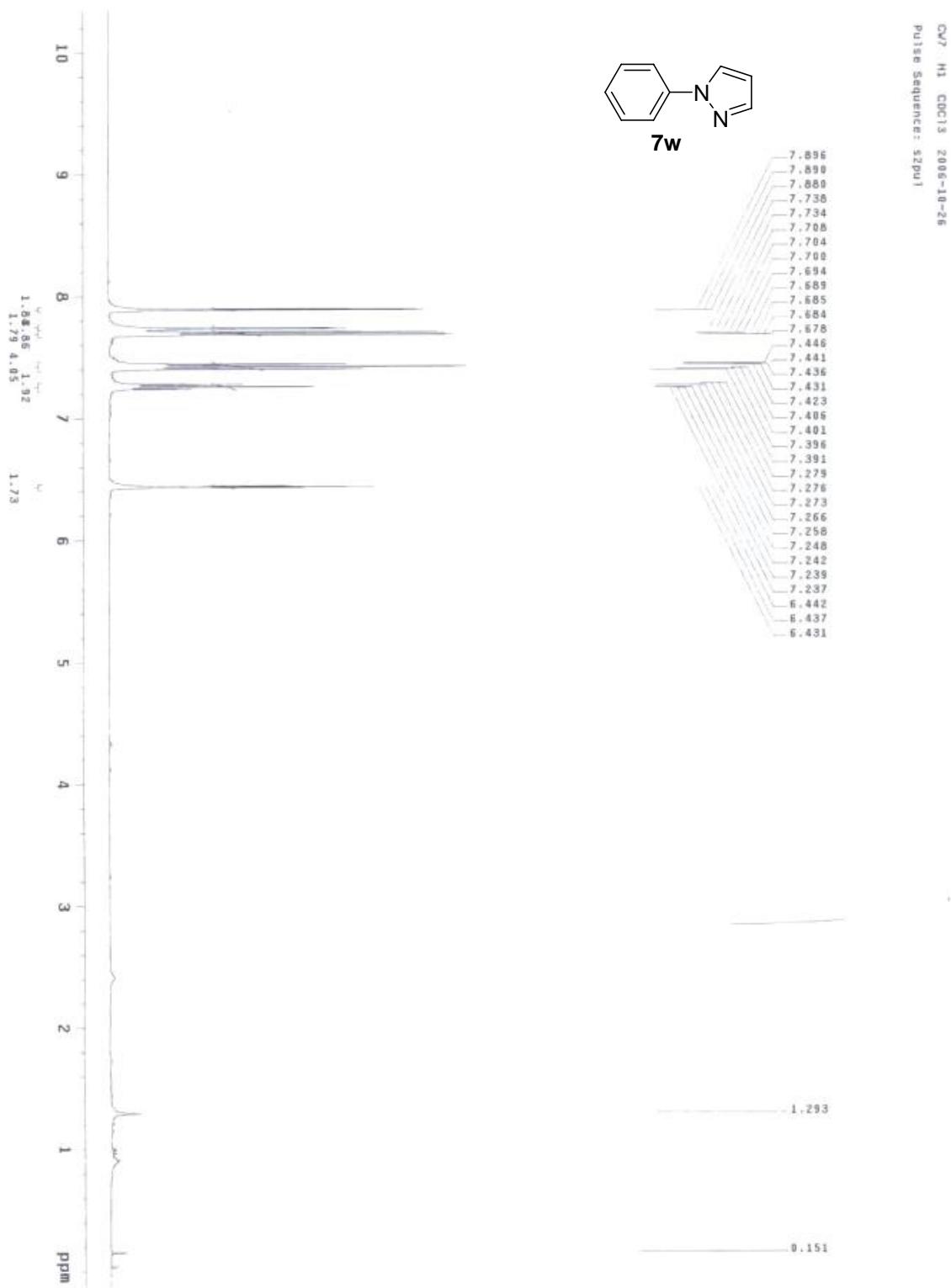


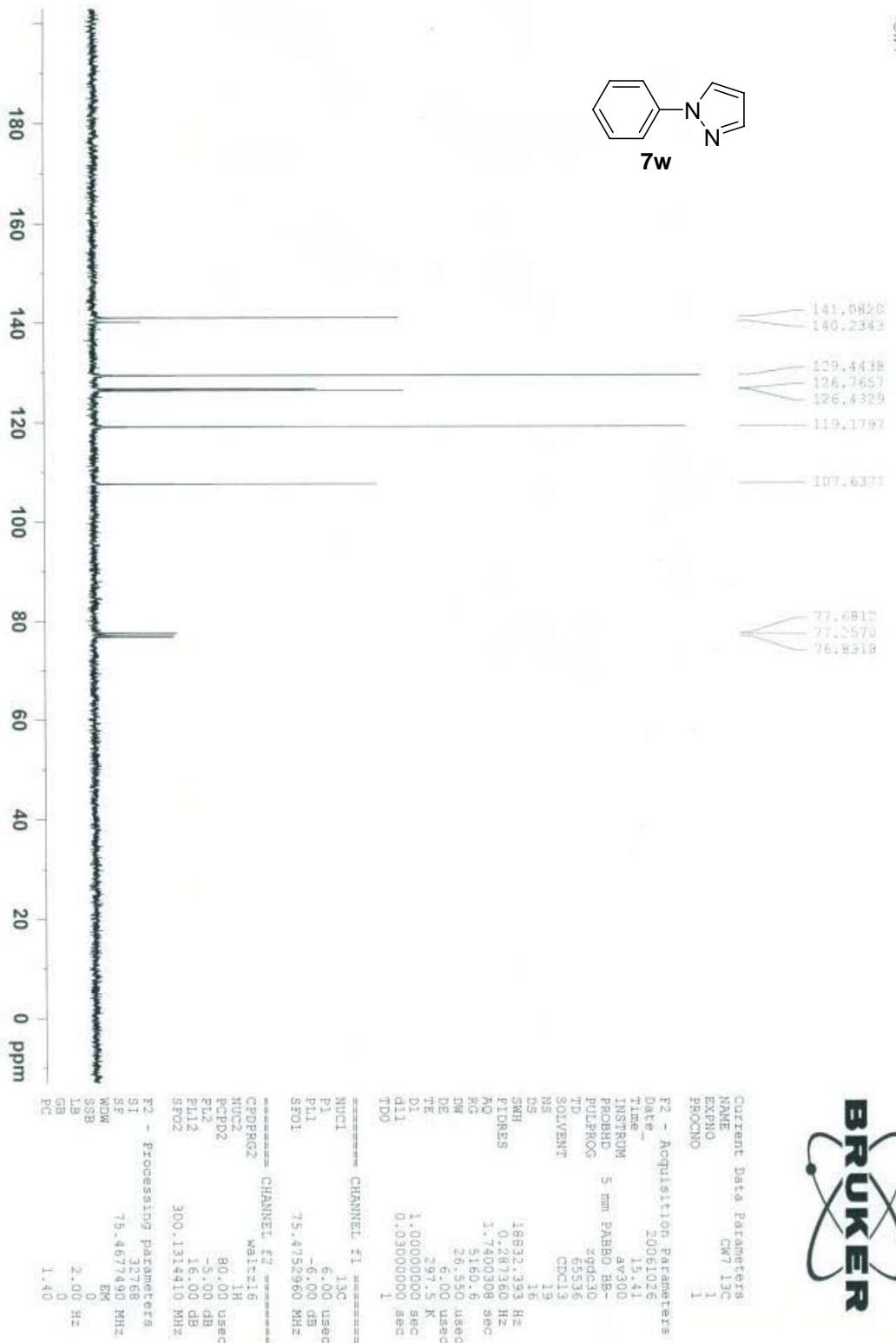
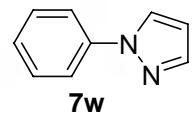
YJS-0006-9
Pulse Sequence: $\pi/2\mu\text{s}$

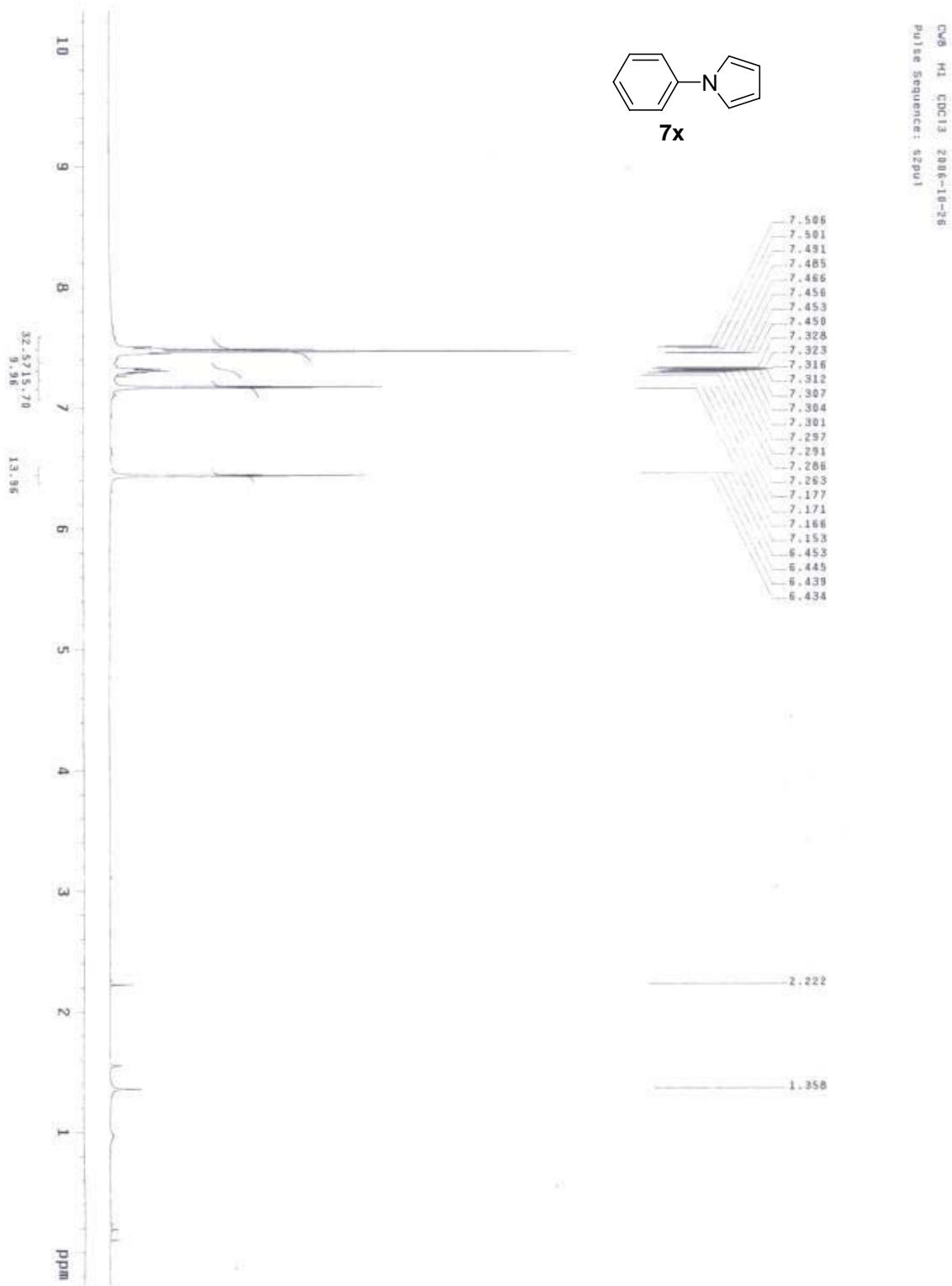


7v

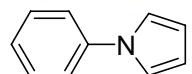








CWB

**7x**