

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.

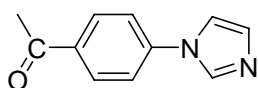
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by refluxing for at least 24 h over CaH_2 (chloroform, DMF or DMSO), sodium/benzophenone (THF or toluene), and freshly distilled prior to use. CuI should be washed with 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 $^\circ\text{C}$ for 24 h. The reaction mixture was then cooled to

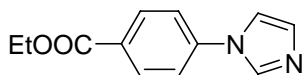
ambient temperature, diluted with 2-3 mL of ethyl acetate, filtered through a plug of silica gel, and washed with 10-20 mL of ethyl acetate. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

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



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

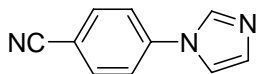
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 4-bromoacetophenone (0.239 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (99% yield). ¹H NMR (600 MHz, 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

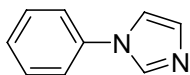
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with ethyl 4-bromobenzoate (196 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white

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^+]



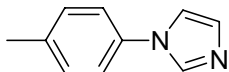
4-Imidazol-1-yl-benzonitrile (7d)²

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^+].



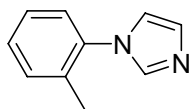
1-Phenyl-1H-imidazole (7a)²

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^+].



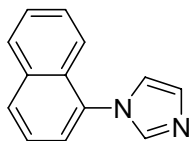
1-(4-Tolyl)-1H-imidazole (7e)²

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⁺].



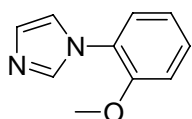
1-(2-Tolyl)-1H-imidazole (7f)¹

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 (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⁺]



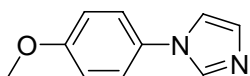
1-Naphthalen-1-yl-1H-imidazole (7g)¹

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

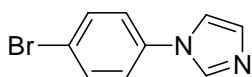
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromoanisole (149 μ L, 1.2 mmol) for 48 h at 110 °C in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (64% yield). ¹H 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

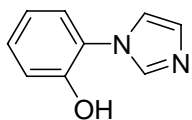
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with

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). ^1H NMR (600 MHz, CDCl_3): 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, CDCl_3): 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

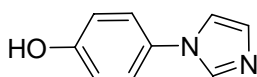
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 1,4-dibromobenzene (0.283 g, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a white solid (87% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.23-7.30 (m, 4H), 7.61 (m, 2H), 7.85 (bs, 1H) ppm. ^{13}C NMR (150 MHz, CDCl_3): 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

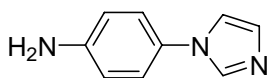
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromophenol (127 μ L, 1.2 mmol) in the presence of ligand **4a** for 48 h. The crude reaction mixture was dissolved in 20 mL of 2 M HCl, and washed once with diethyl ether. The aqueous layer was brought to pH = 7.5 with NaHCO_3 , and extracted repeatedly with

CH₂Cl₂. The combined organic layer was dried with anhydrous MgSO₄, 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, CD₃OD): 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. ¹³C NMR (150 MHz, CD₃OD and CDCl₃): δ 116.7, 119.3, 124.7, 128.1, 149.9 ppm. MS (ESI⁺) *m/z* 161 [M+1]⁺.



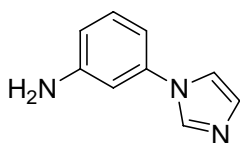
4-Imidazol-1-ylphenol (7l)¹

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 Na₂CO₃, and extracted repeatedly with CH₂Cl₂. The combined organic layer was dried with anhydrous MgSO₄, 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, CD₃OD): 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. ¹³C NMR (150 MHz, CD₃OD): δ 117.3, 120.3, 124.2, 129.7, 130.7, 137.1, 158.5 ppm. GC-MS (EI, *m/z*): 160 [M⁺].



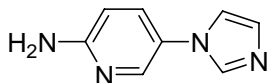
4-Imidazol-1-yl-phenylamine (7m)

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, CDCl₃): δ 3.58 (bs, 2H), 6.74 (s, 1H), 6.75 (s, 1H), 7.15-7.27 (m, 4H), 7.74 (s, 1H) ppm. ¹³C NMR (150 MHz, CDCl₃): 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

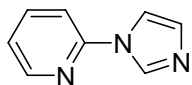
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 3-bromoaniline (131 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give a light yellow solid (85% yield). ¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (75 MHz, CDCl₃): 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)

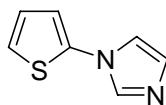
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with

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, CDCl₃): 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. ¹³C NMR (75 MHz, CDCl₃): 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

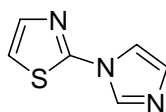
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromopyridine (117 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (98% yield). ¹H NMR (300 MHz, CDCl₃): 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. ¹³C NMR (75 MHz, CDCl₃): 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

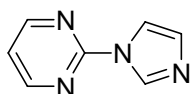
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromothiophene (115 μL, 1.2 mmol) in the presence of ligand **4a**. The crude product was

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 $[\text{M}^+]$.



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

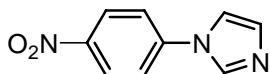
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-bromothiazole (106 μL , 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give pale yellow oil (85% yield). ^1H NMR (400 MHz, CDCl_3): 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 $[\text{M}^+]$.



2-(1H-imidazol-1-yl)pyrimidine (7s)⁵

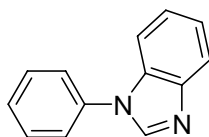
Following the general procedure, imidazole (0.068 g, 1.0 mmol) was coupled with 2-chloropyrimidine (137mg, 1.2 mmol) in the presence of ligand **4a**. The crude product was purified over a silica gel column using ethyl acetate/petrol ether (1/1) to give white solid (97% yield). ^1H NMR (400 MHz, CDCl_3): 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^+].



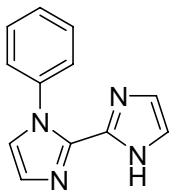
1-(4-Nitrophenyl)-1H-imidazole (7t)²

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^+].



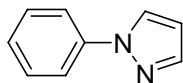
1-Phenyl-1H-benzimidazole (7u)⁶

Following the general procedure, benzimidazole (0.118 g, 1.0 mmol) was coupled with bromobenzene (126 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 (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^+].



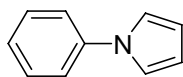
2-(1H-Imidazol-2-yl)-1-phenyl-1H-imidazole (7v)

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). ^1H NMR (600 MHz, CDCl_3): 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, CDCl_3): δ 123.4, 126.3, 127.7, 128.6, 128.9, 138.1, 138.1, 139.2 ppm. GC-MS (EI, m/z): 209 $[\text{M}-1]^+$.



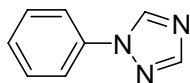
1-Phenyl-1H-pyrazole (7w)⁷

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). ^1H NMR (400 MHz, CDCl_3): 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, CDCl_3): δ 107.6, 119.2, 126.4, 126.8, 129.4, 140.2, 141.1 ppm. GC-MS (EI, m/z): 144 $[\text{M}^+]$.



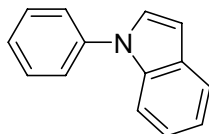
1-Phenyl-1H-pyrrole (7x)⁸

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). ¹H 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. ¹³C 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). ¹H 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. ¹³C 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⁺].



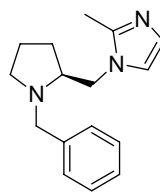
1-Phenyl-1H-indole (7z)⁸

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). ^1H NMR (300 MHz, CDCl_3): 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, CDCl_3): 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^+].

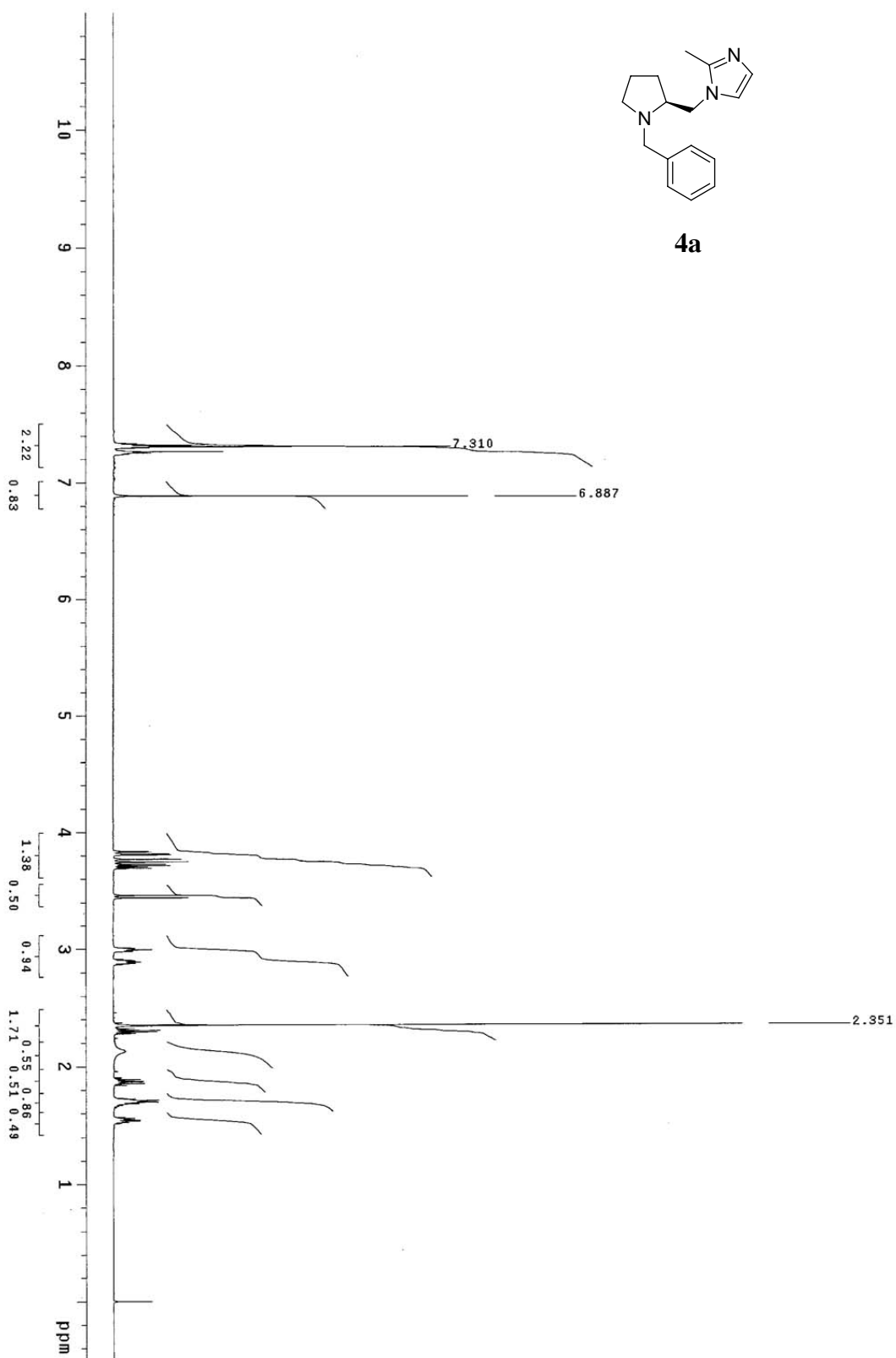
IV. References

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- (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.

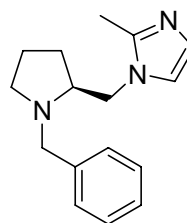
V. Copies of ^1H and ^{13}C NMR spectra for compounds **4a-4c**, **3a-3b**, **2a-2b** and **7a-z**



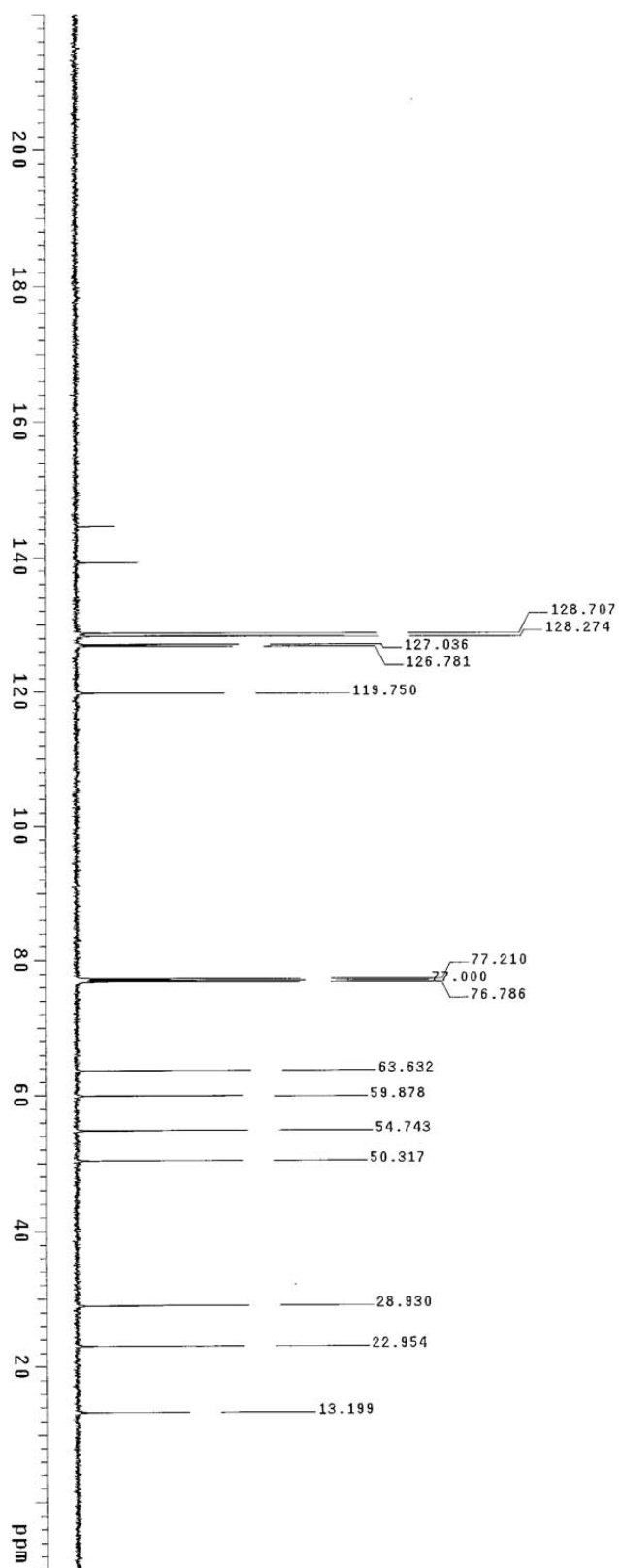
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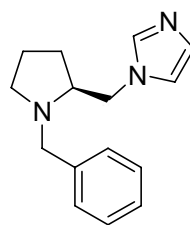


VJS-0606-6
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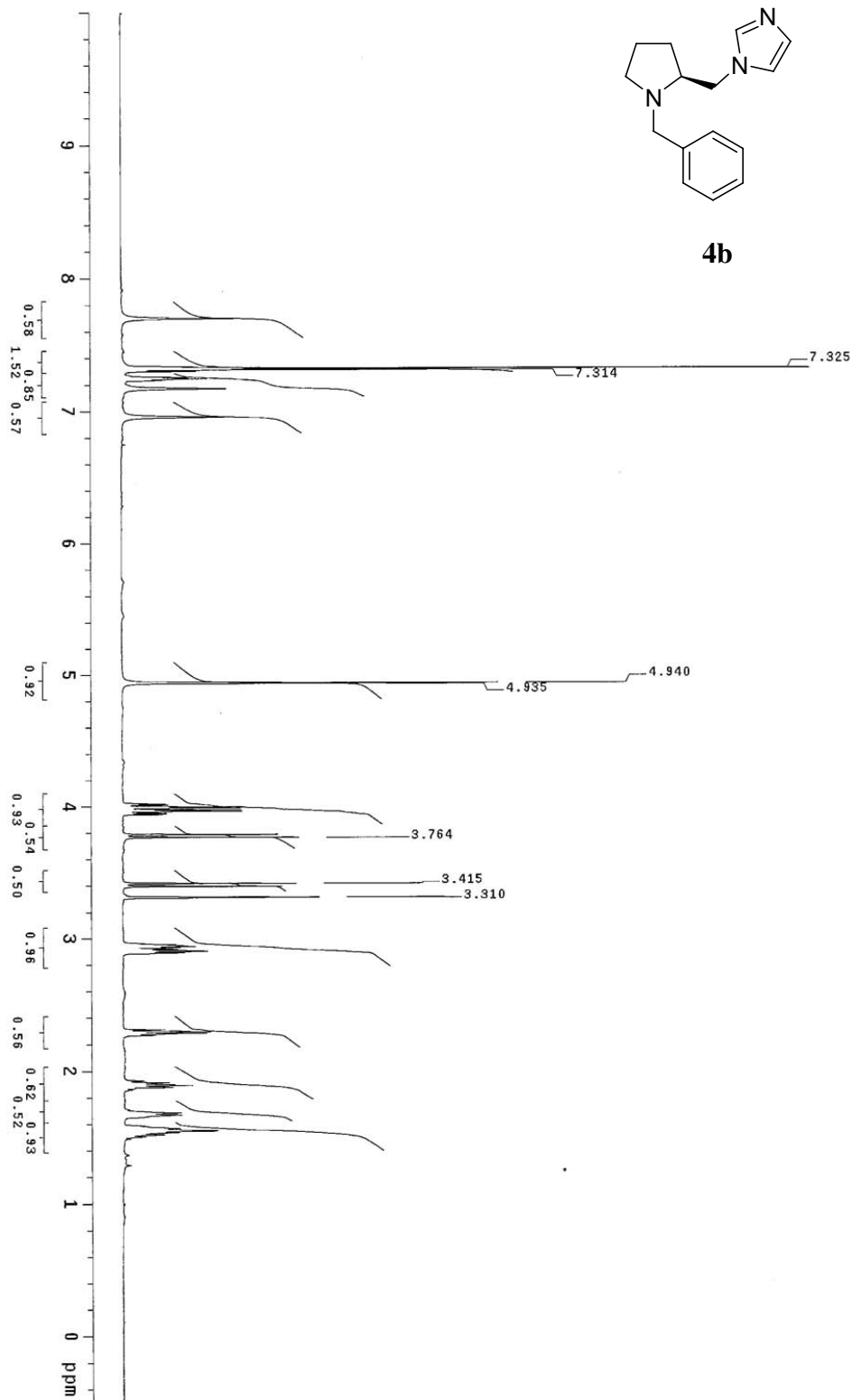


4a

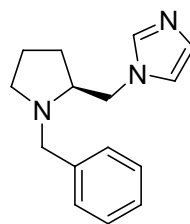




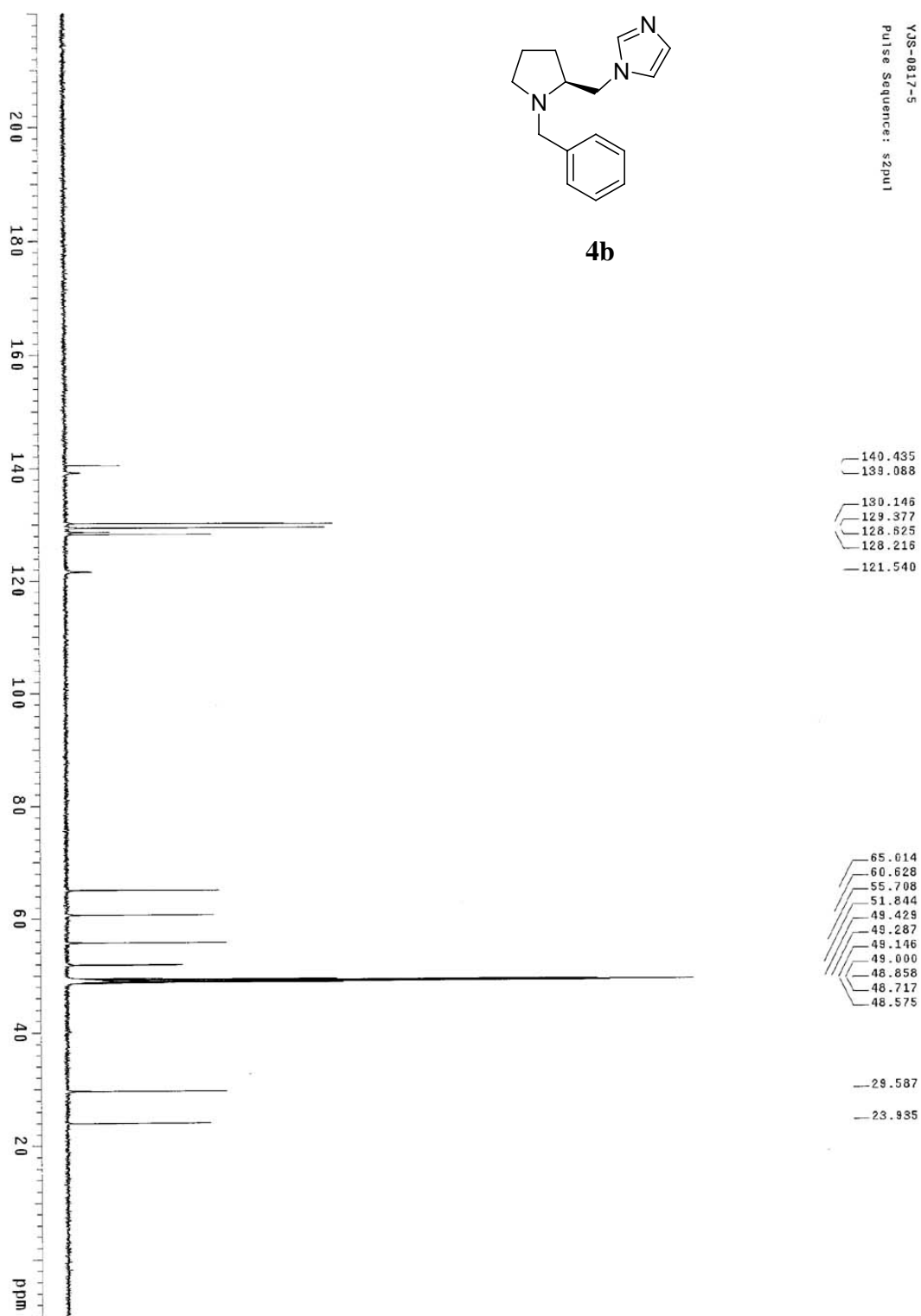
4b



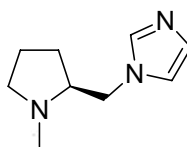
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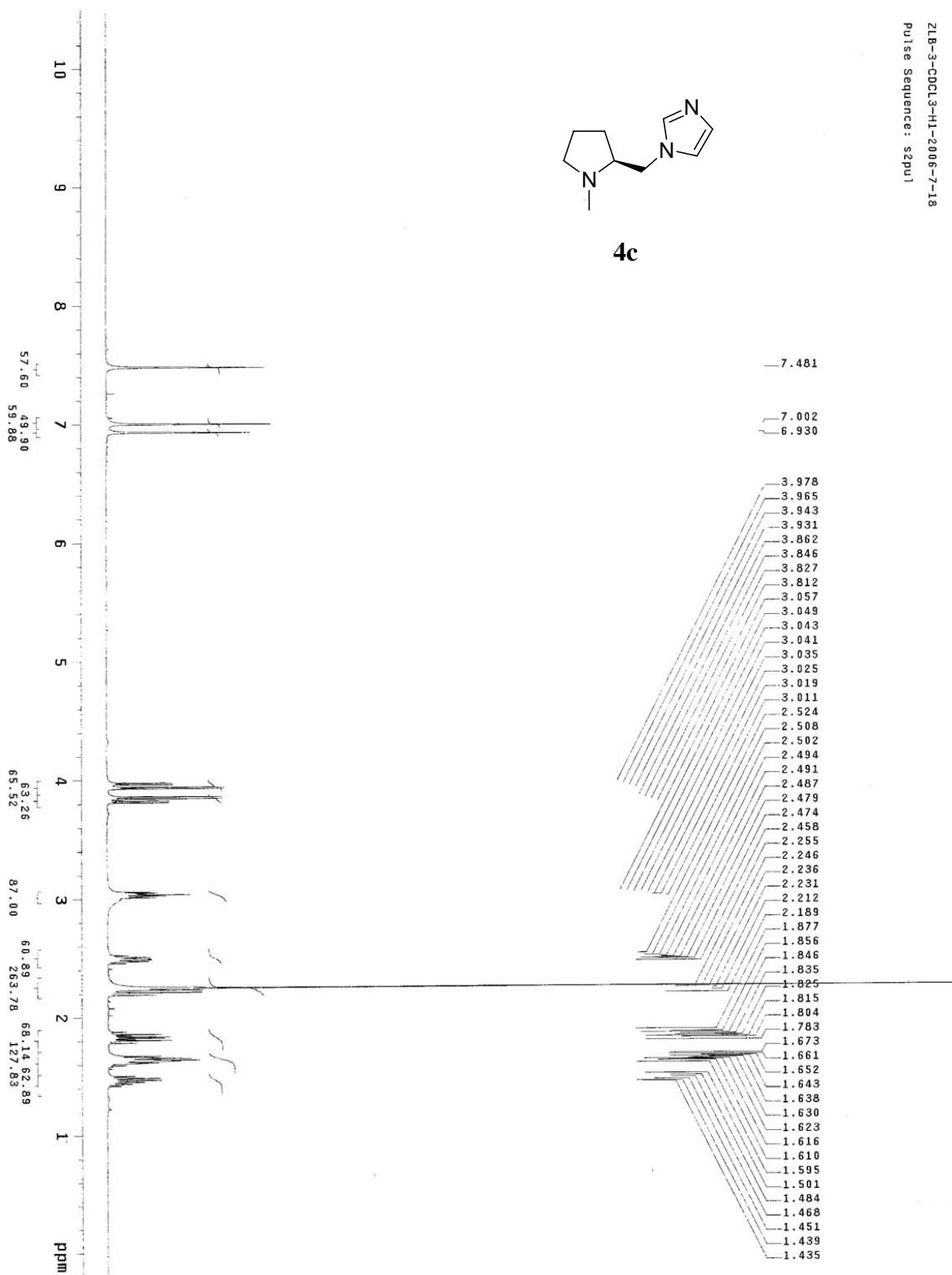
4b

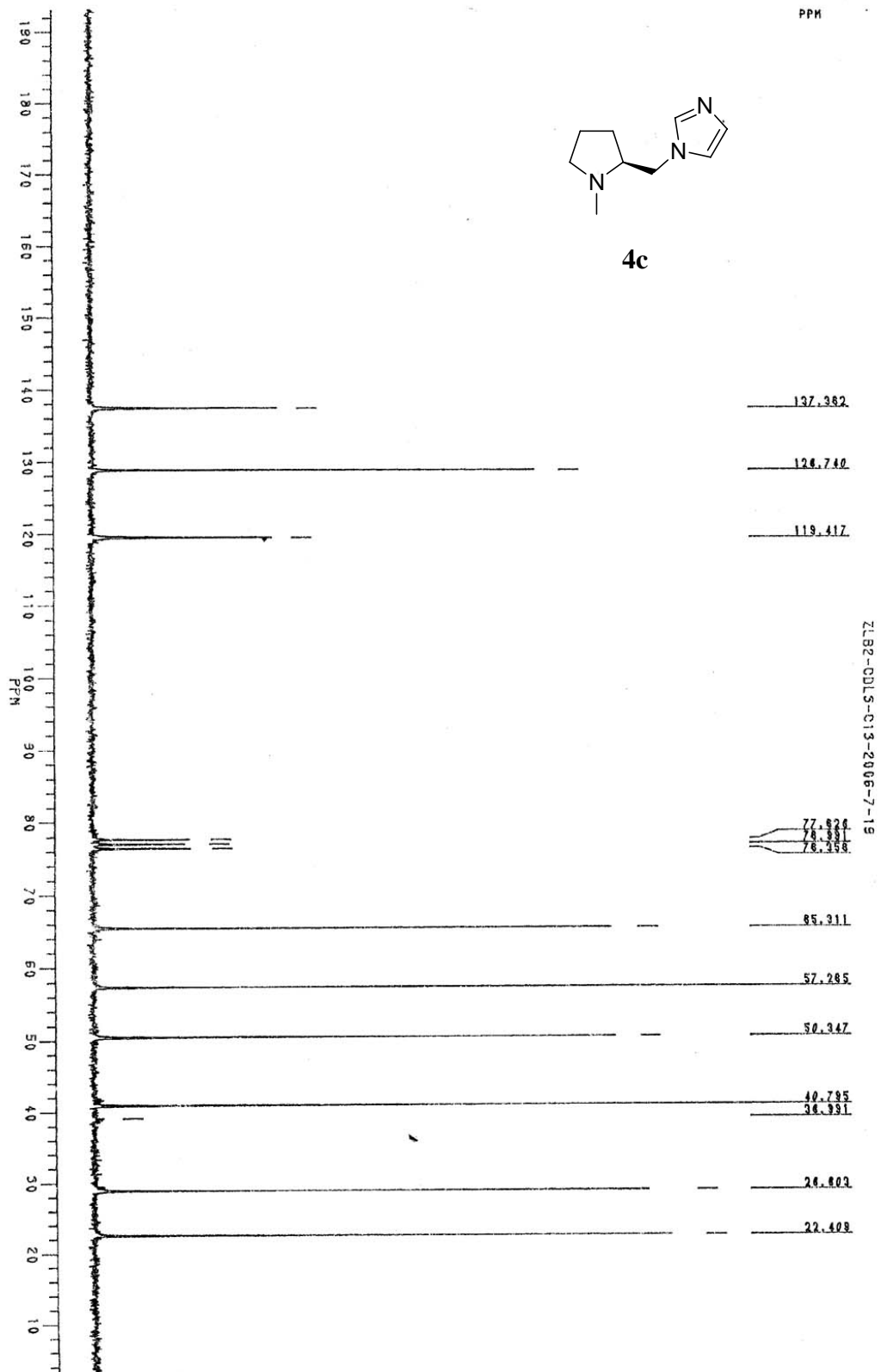


ZLB-3-CDCL3-H1-2006-7-18
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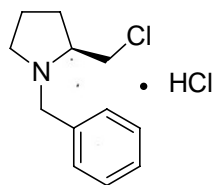


4c

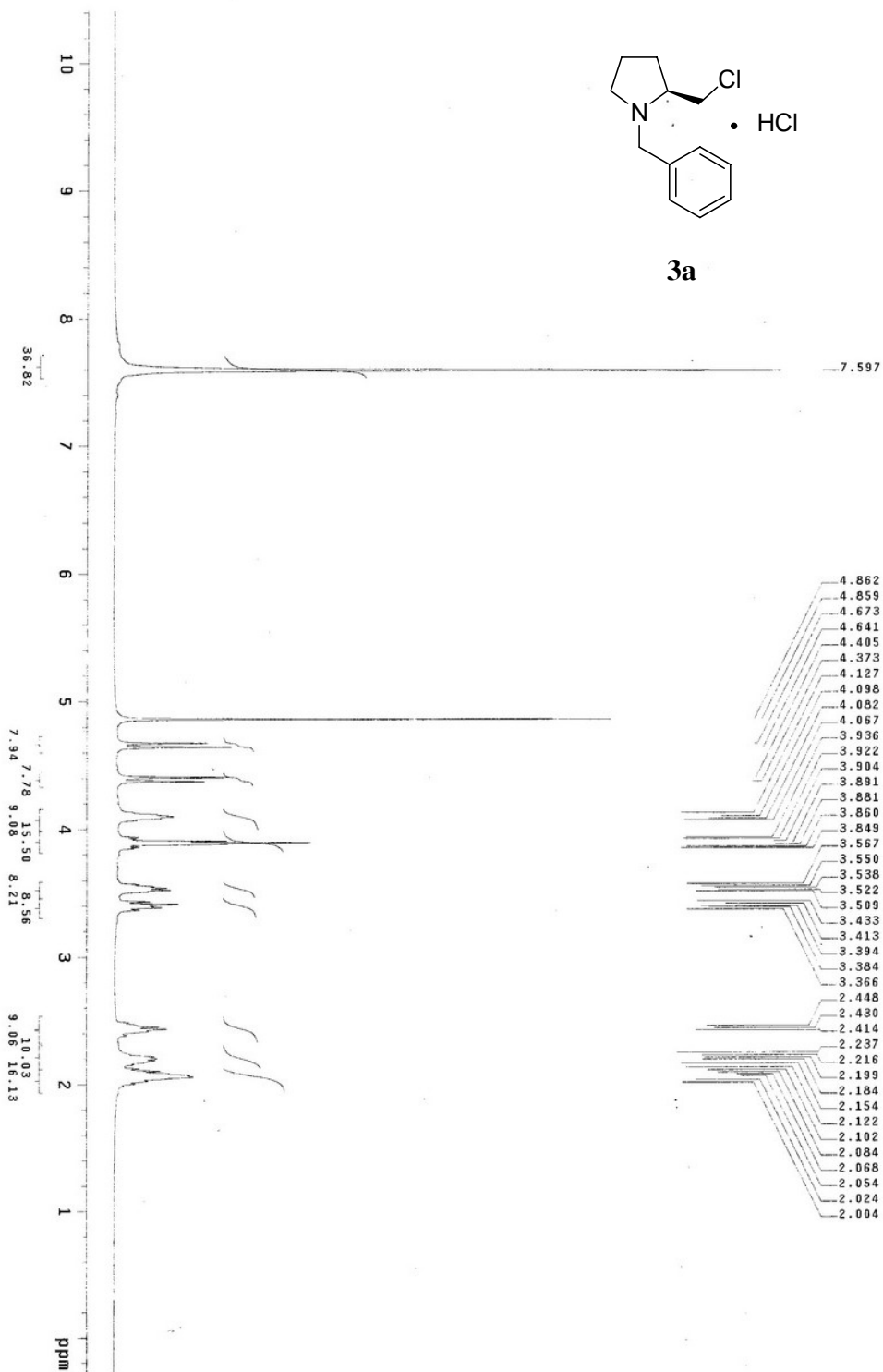




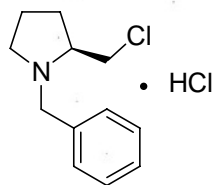
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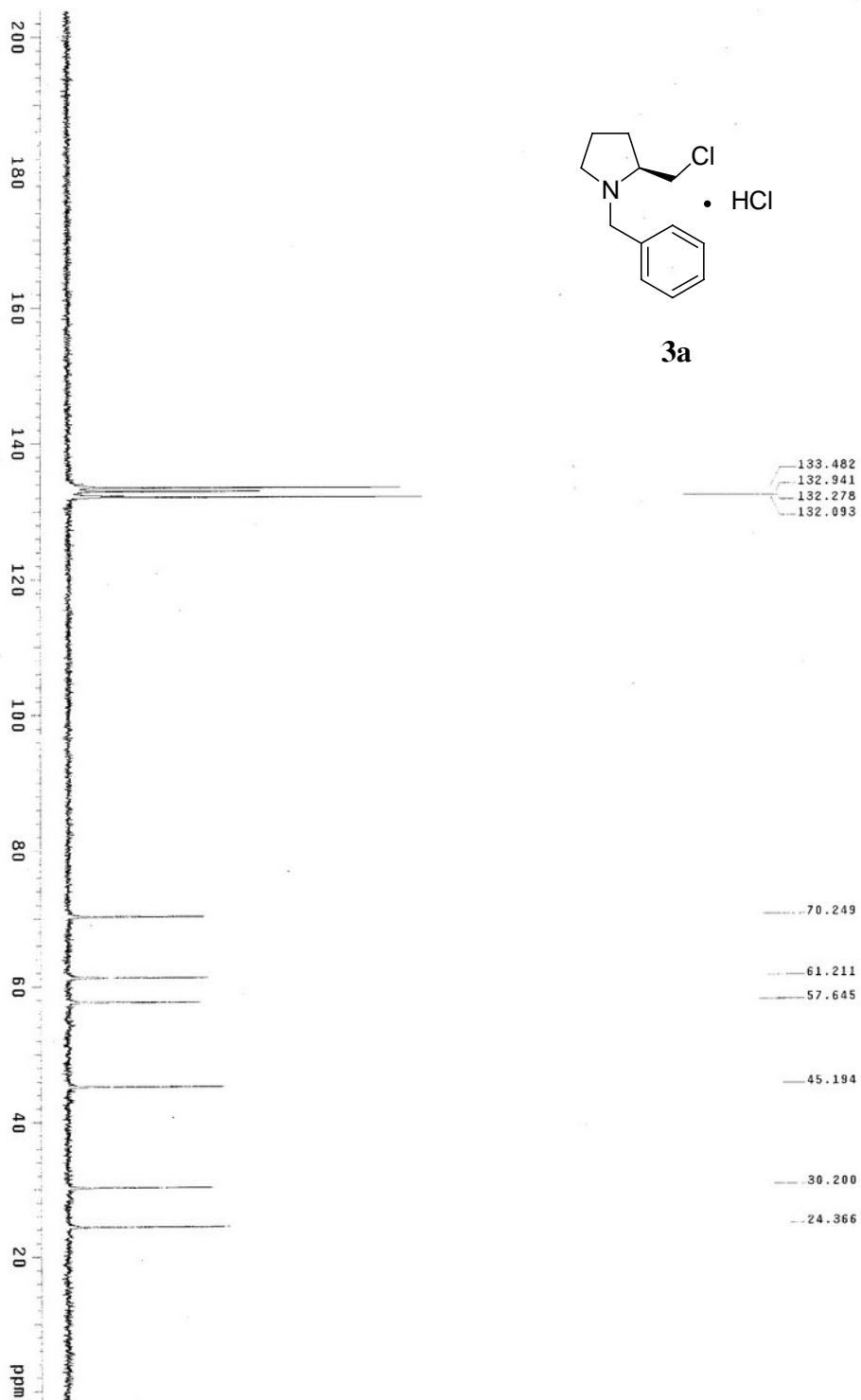
3a

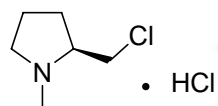


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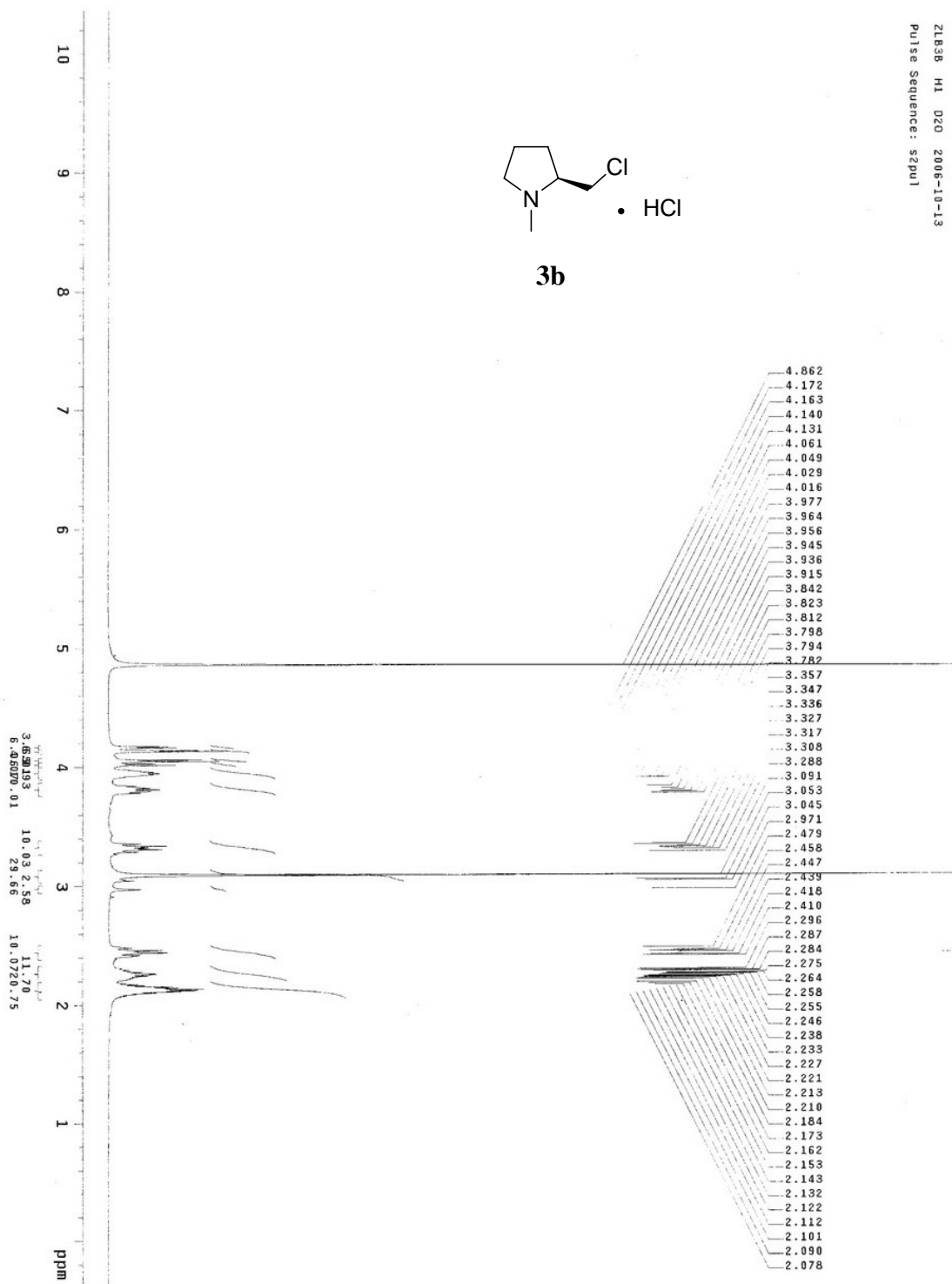


3a

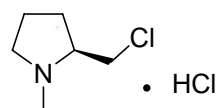




3b



21b38 C13 020 2006-10-17
Pulse Sequence: szpul



3b



71.763

59.889

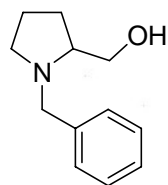
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43.143

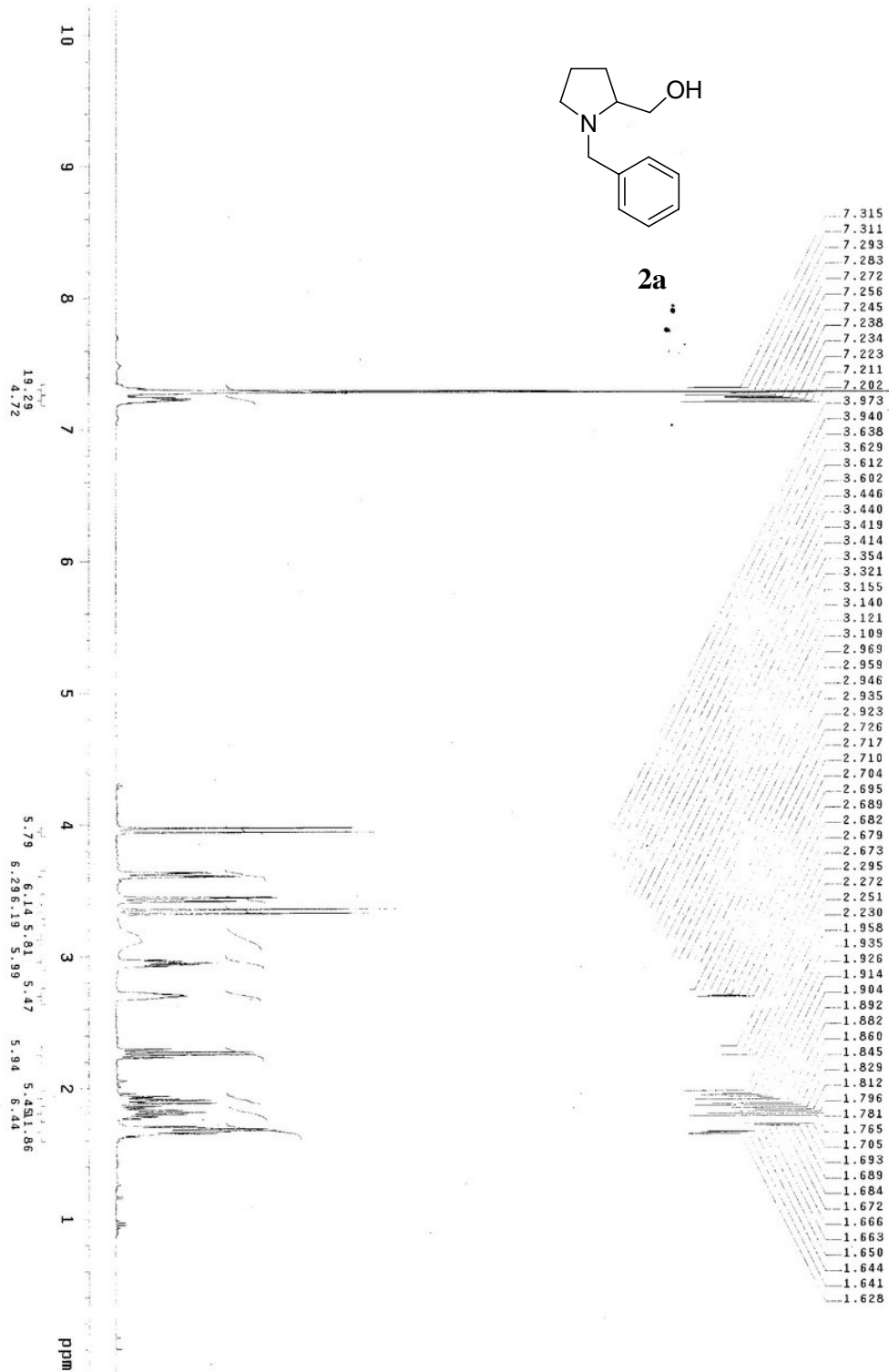
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24.432

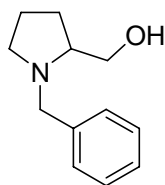
ZLB2A H1 CUC13 2006-10-13
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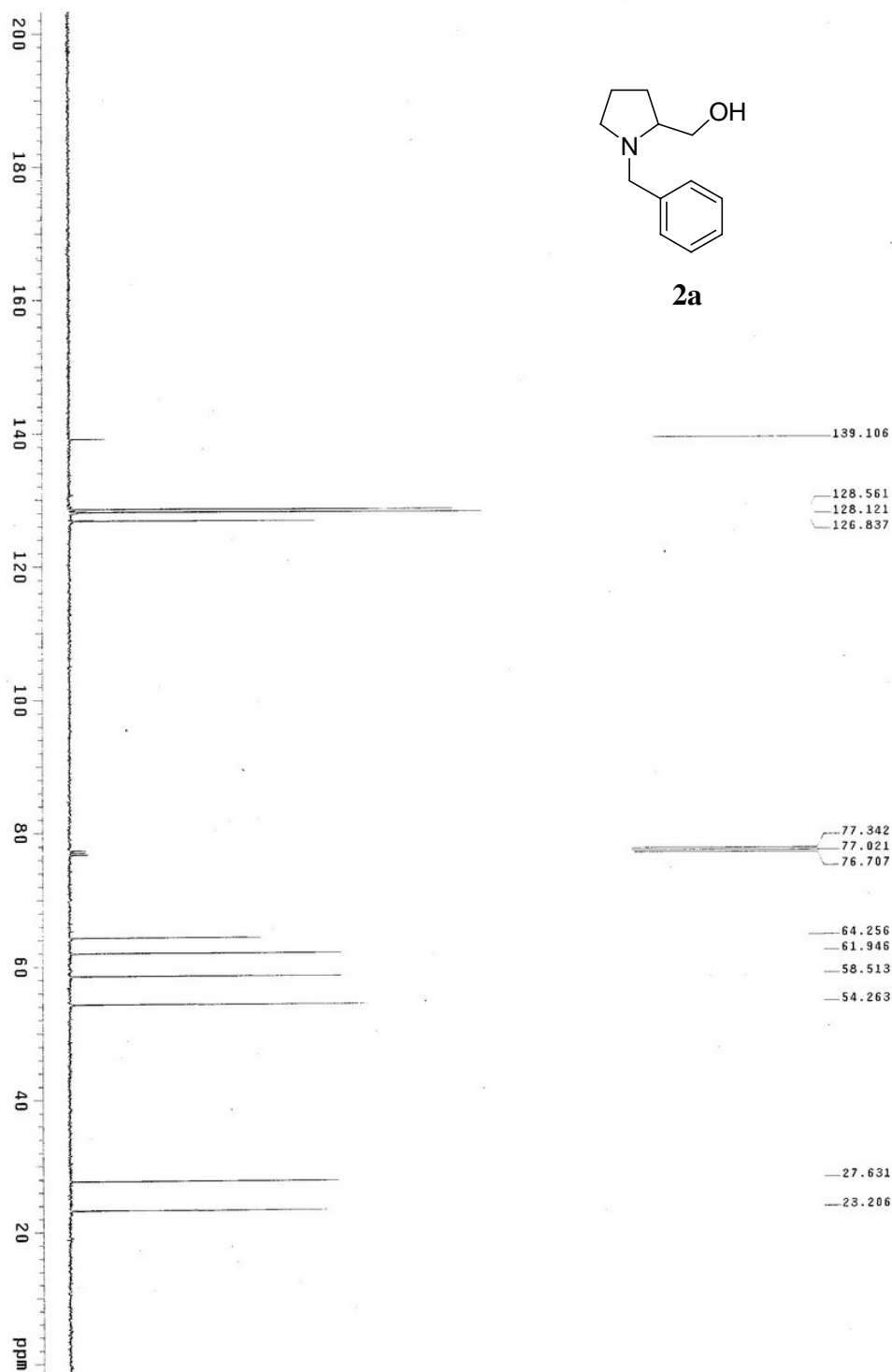
2a



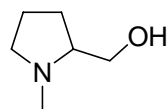
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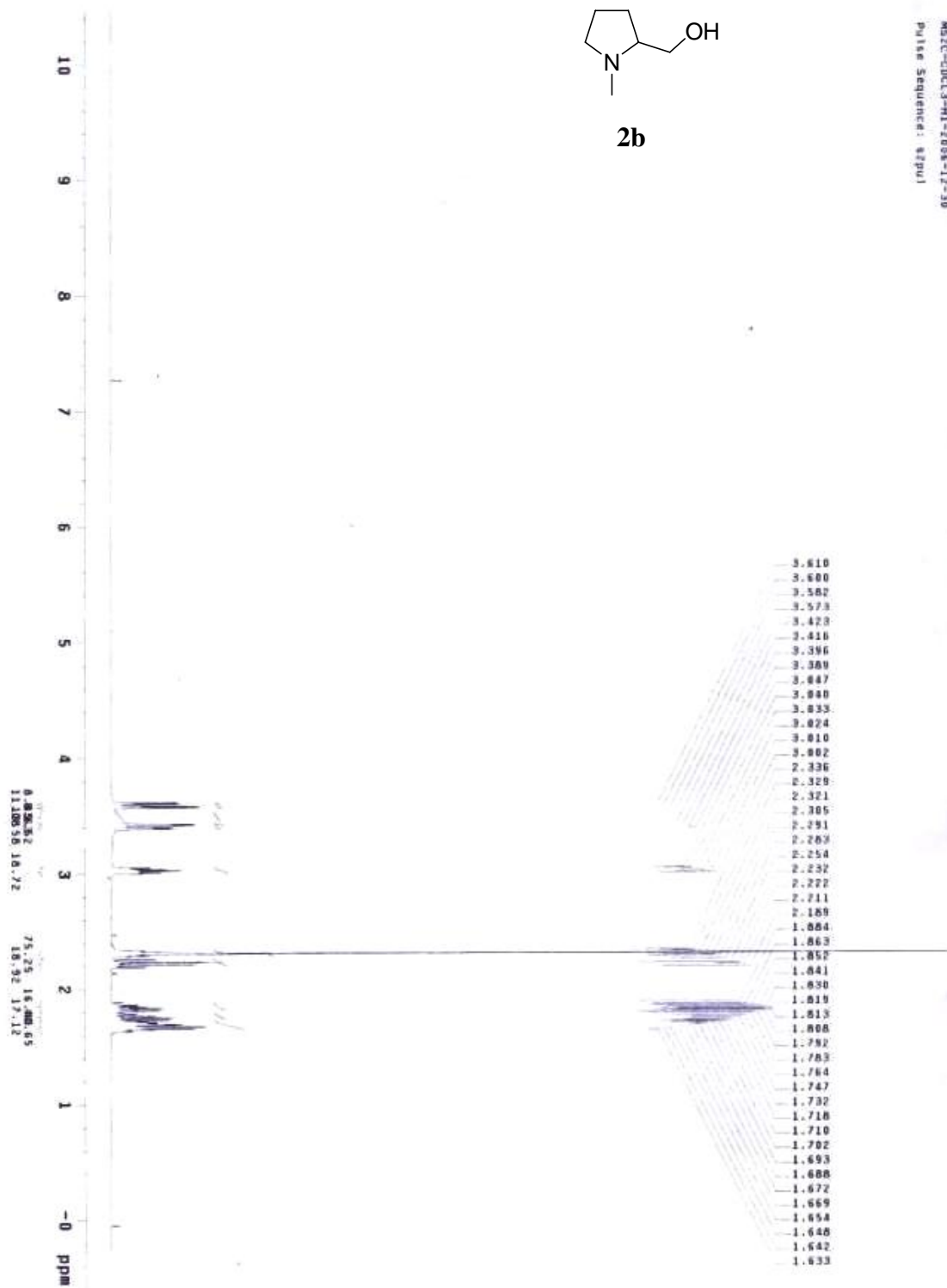
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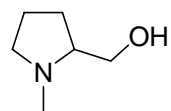
MS-CDC-3-M-2008-12-30
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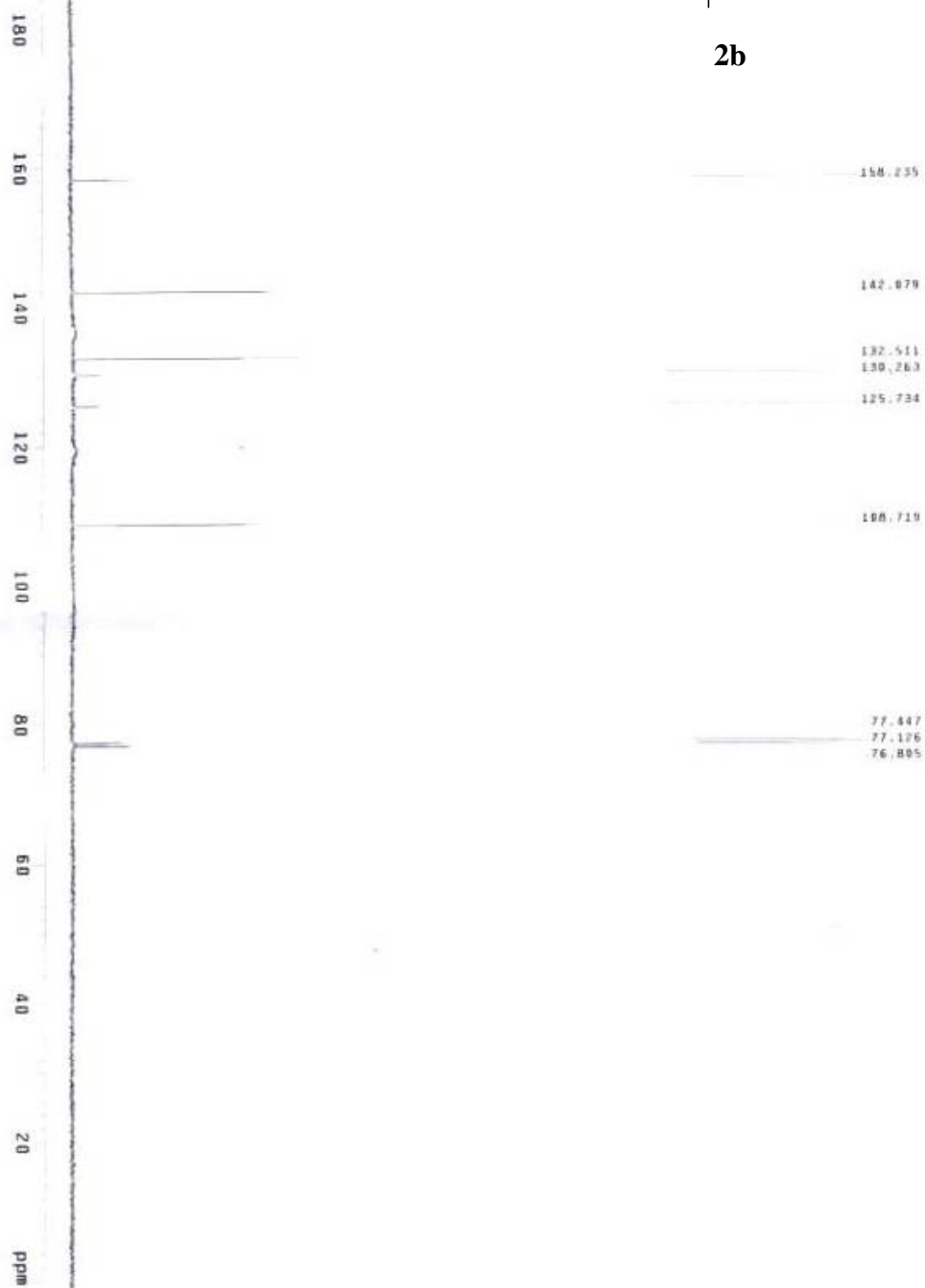
2b



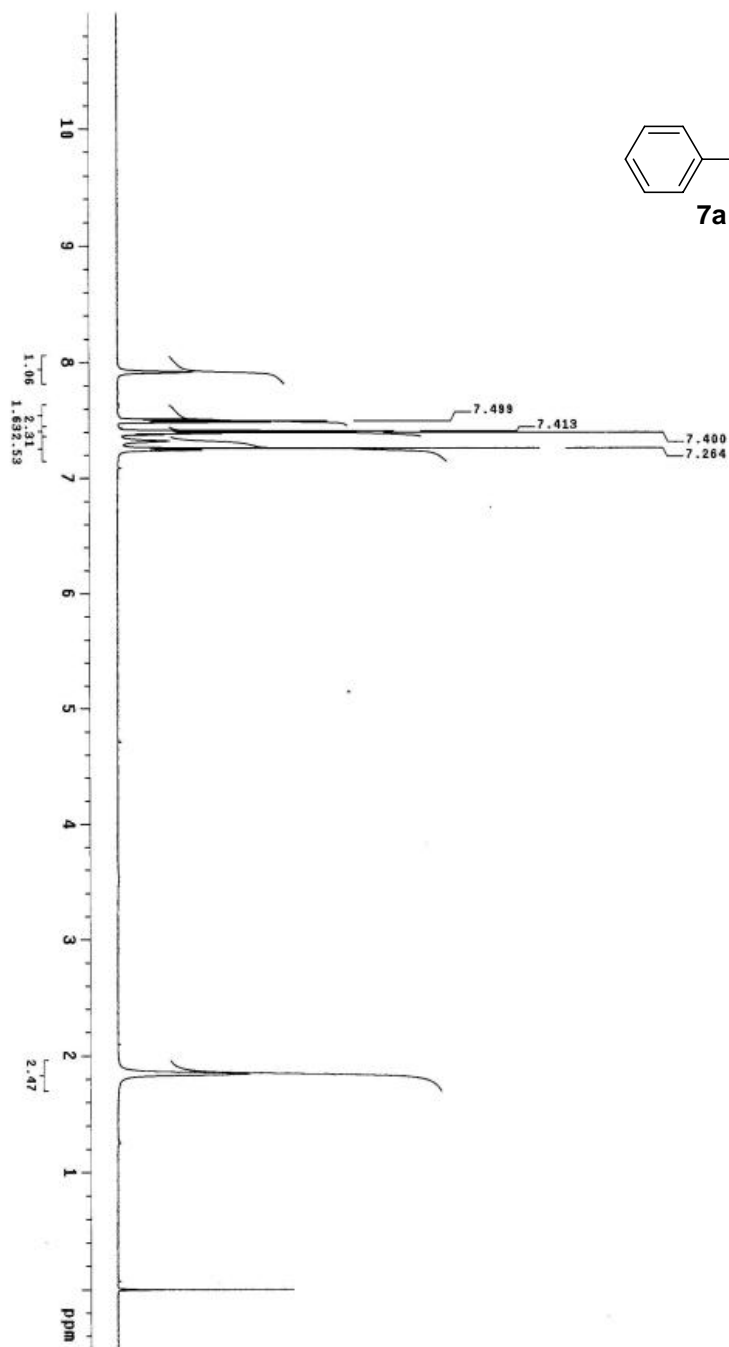
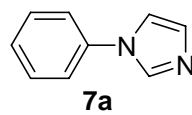
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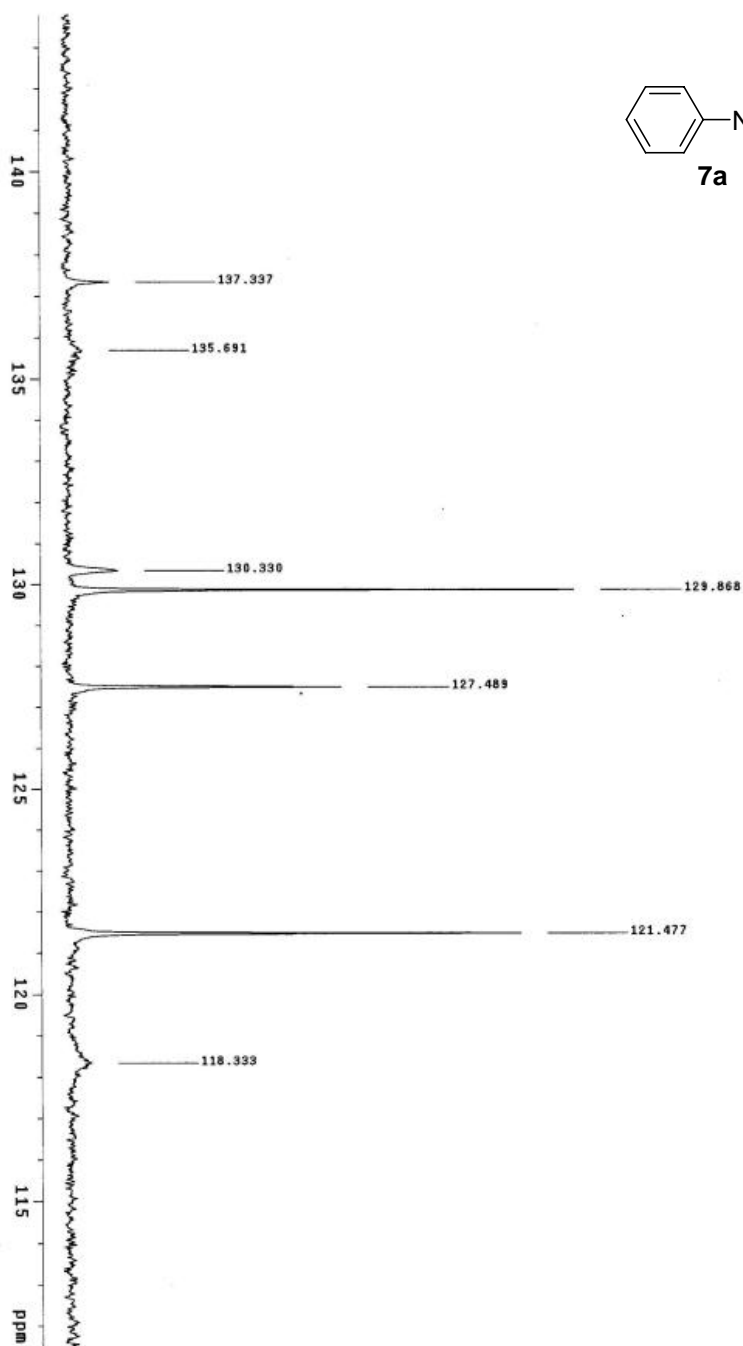
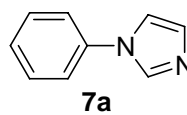
2b



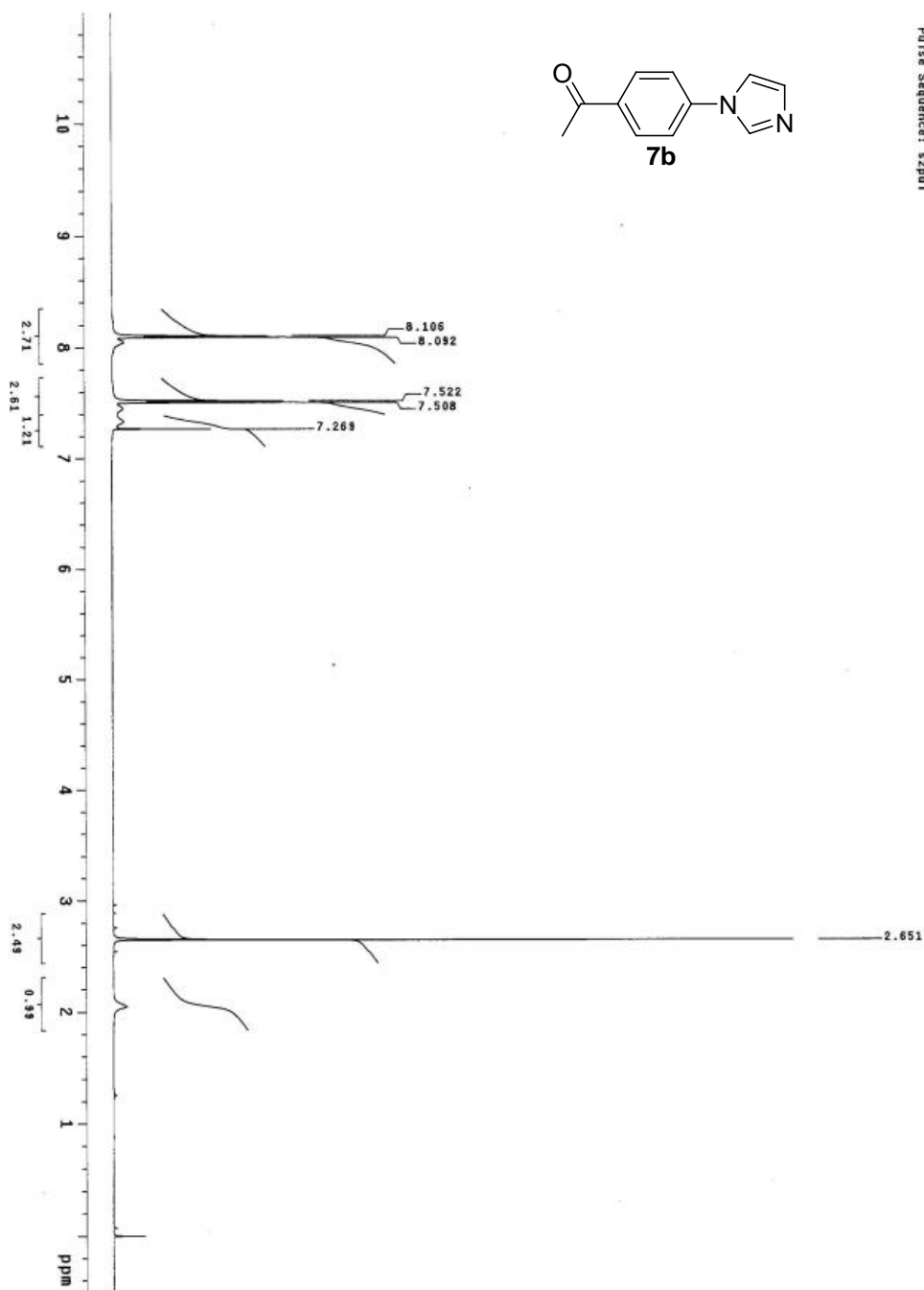
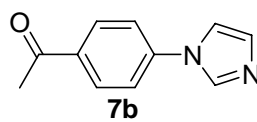
VJS-0606-21
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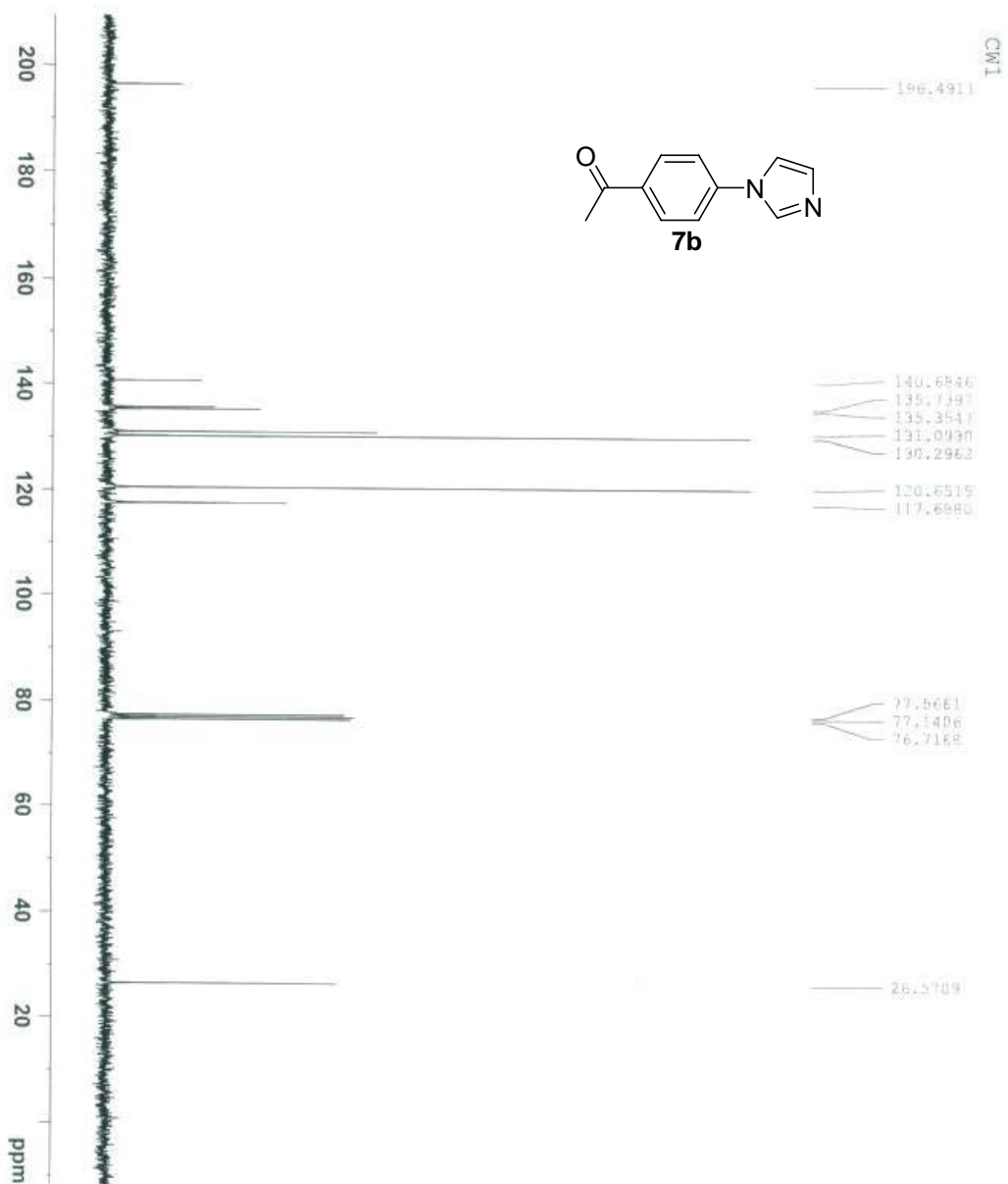


VJS-0605-21
Pulse Sequence: szput



VJS-0606-18
Pulse Sequence: szpu1





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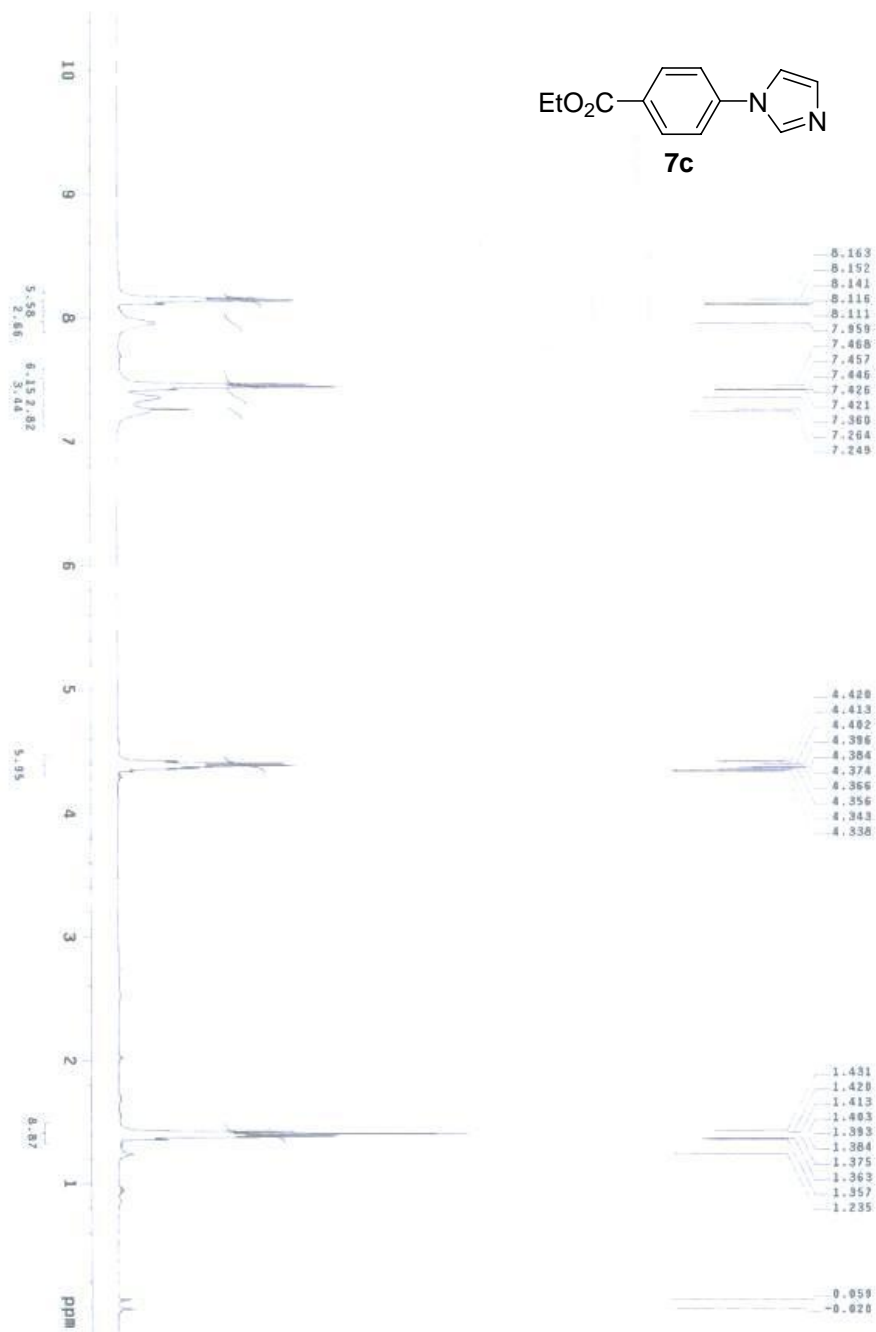
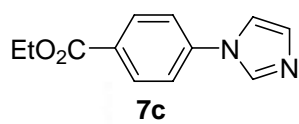
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PULPROG : zgpg30
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SOLVENT : CDCl3
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DS : 16
SWH : 18832.393 Hz
FIDRES : 0.287360 Hz
AQ : 1.7400308 sec
RG : 5160.6
DE : 26.550 usec
TE : 296.9 K
D1 : 1.00000000 sec
d11 : 0.03000000 sec
TDO : 1

===== CHANNEL f1 =====
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P1 : 6.00 usec
PL1 : -6.00 dB
SFO1 : 75.4752960 MHz

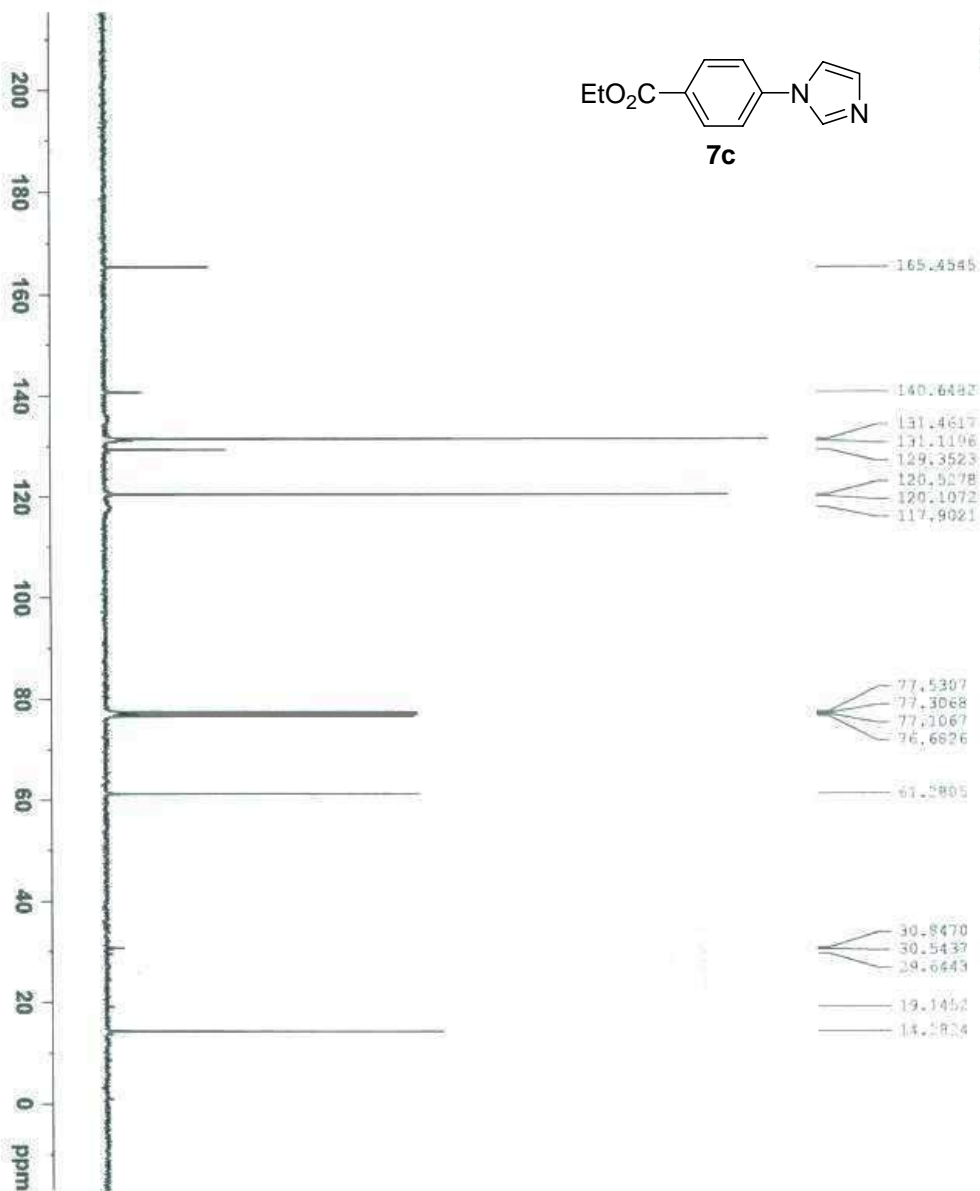
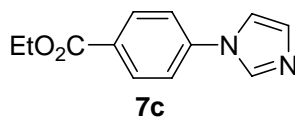
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NUC2 : 1H
PCPD2 : 80.00 usec
PL2 : 3.00 dB
PL12 : 18.00 dB
SFO2 : 300.1314410 MHz

F2 - Processing parameters
SI : 32768
SF : 75.4677490 MHz
WDW : EN
SSB : 0
LB : 2.00 Hz
GB : 0
PC : 1.40
  
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CV3-CDCL3-H1-1886-18-25
Pulse Sequence: zgpg30



CM3



Current Data Parameters
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PROCNO 1

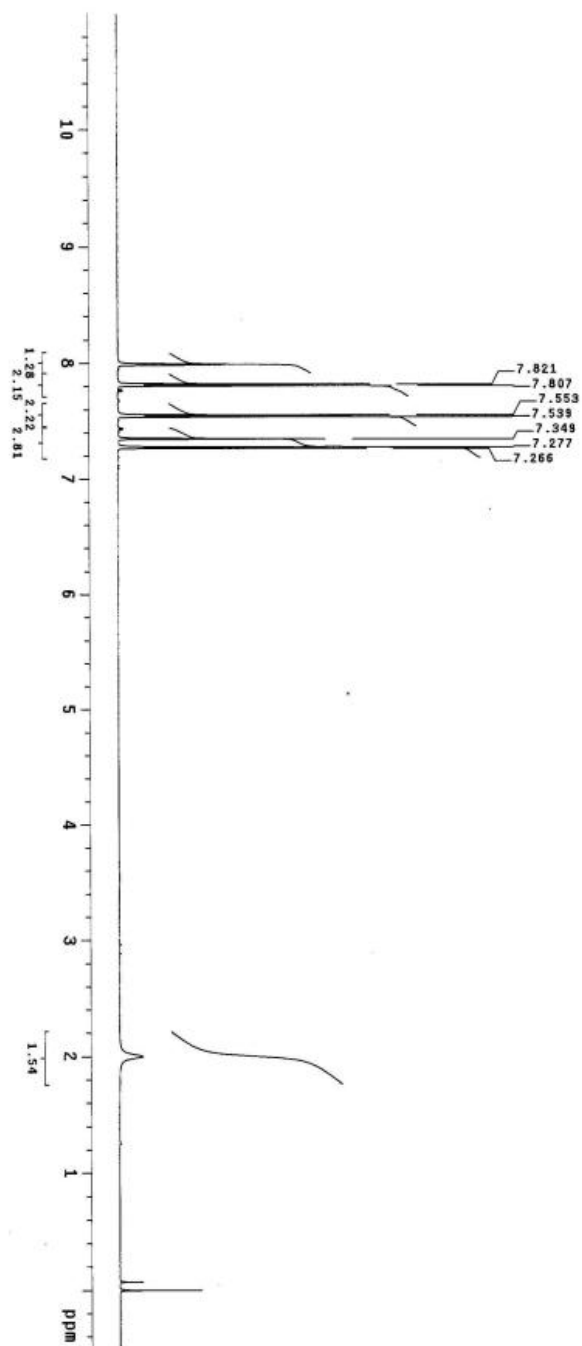
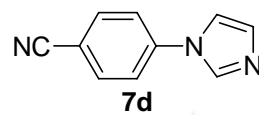
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NS 1048
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AQ 1.7400308 sec
RG 5169.6
RG 26.350 usec
DE 6.00 usec
TE 297.3 K
D1 1.00000000 sec
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===== CHANNEL f1 =====
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PL1 -6.00 dB
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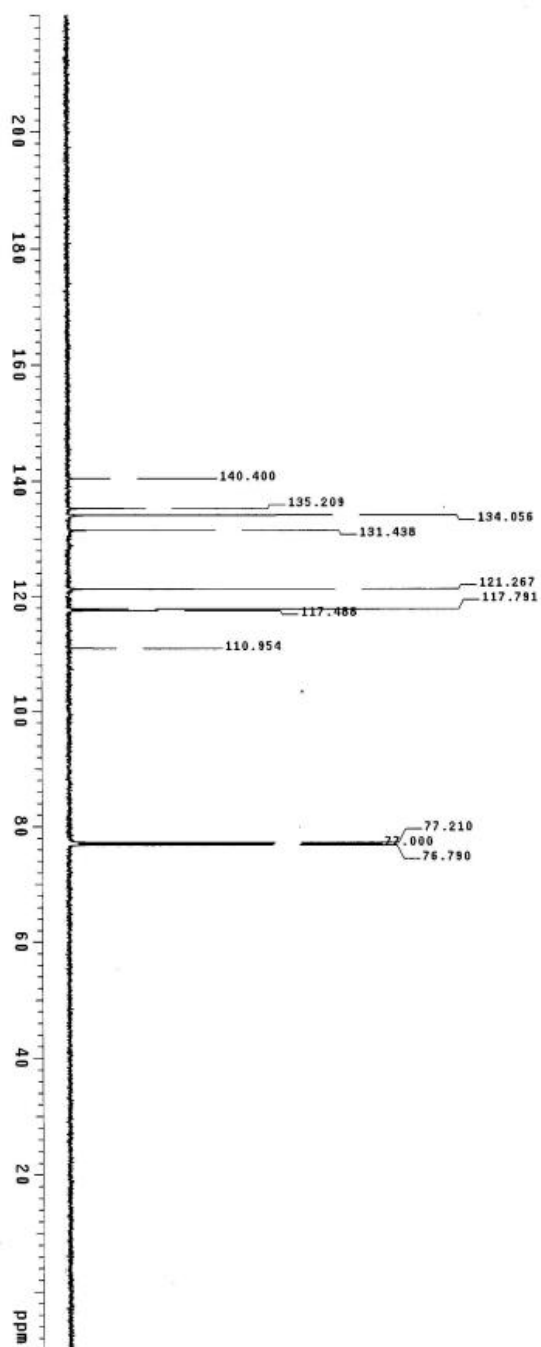
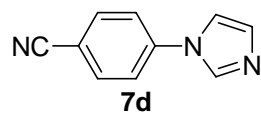
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NUC2 1H
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PL12 16.00 dB
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F2 - Processing parameters
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SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

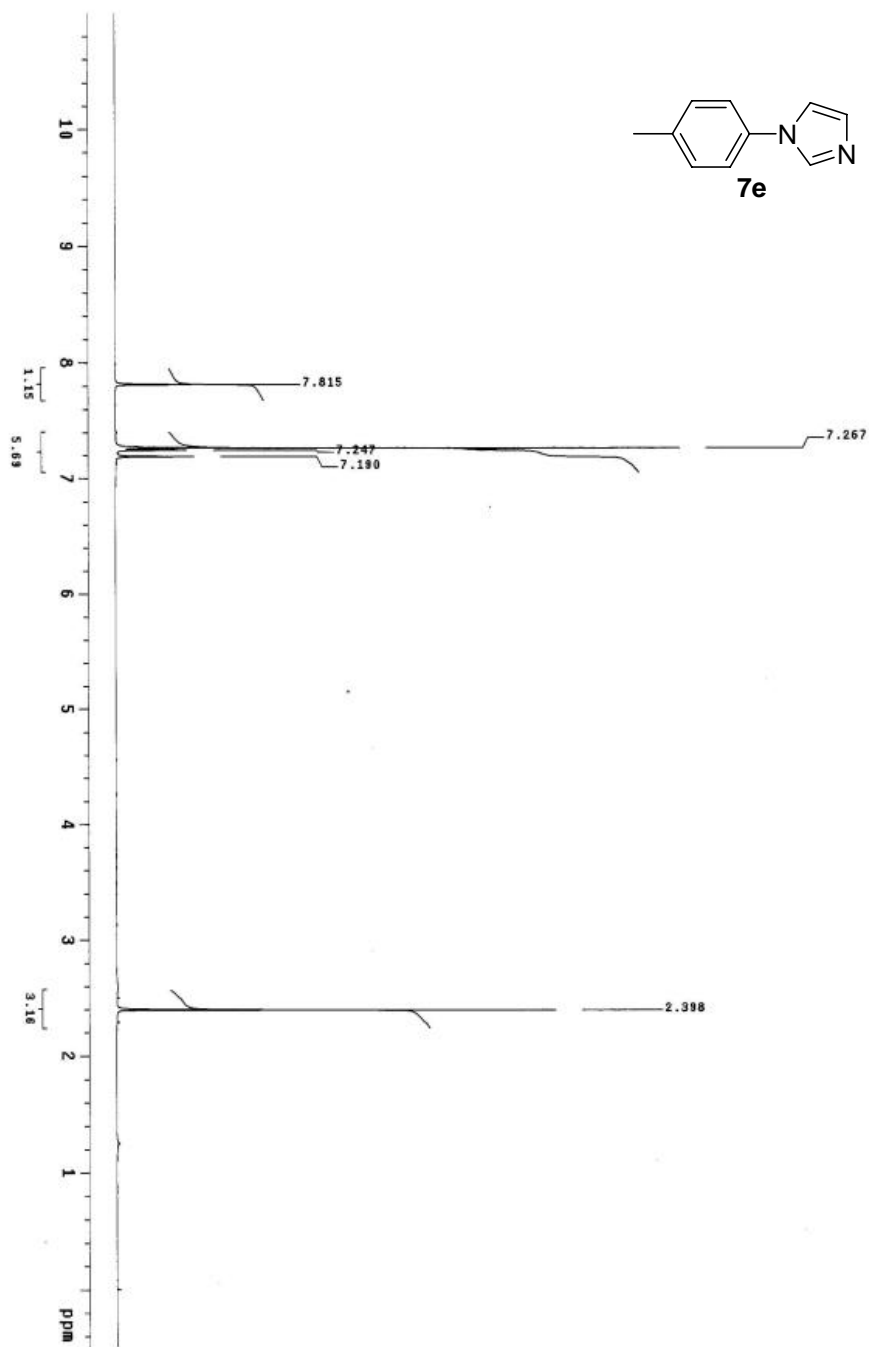
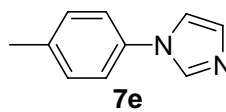
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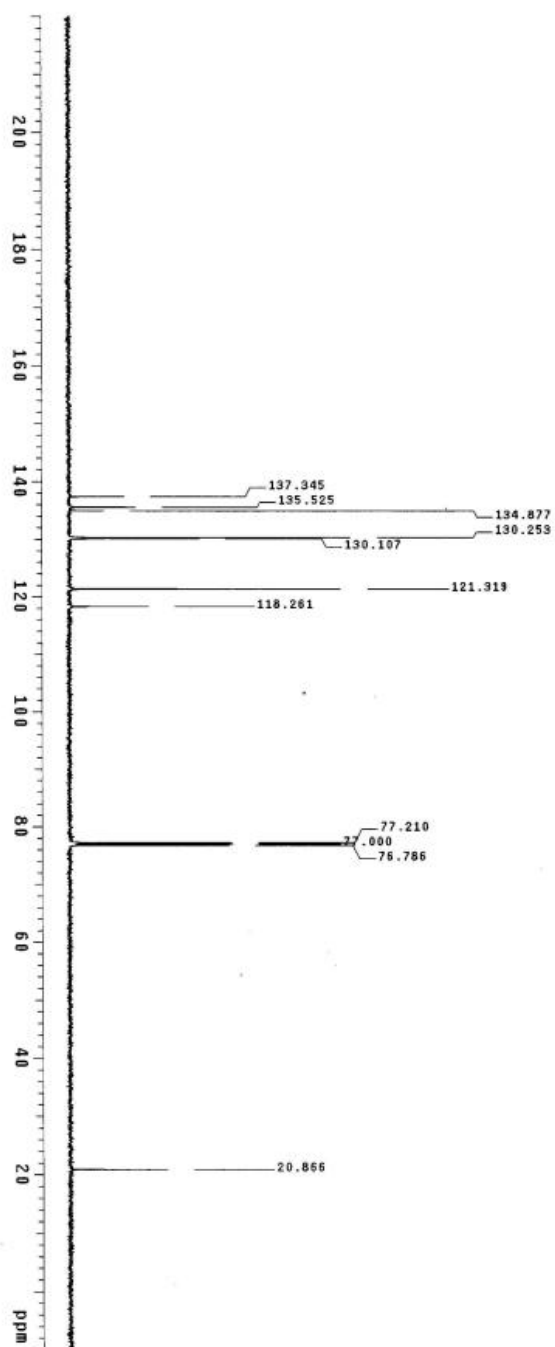
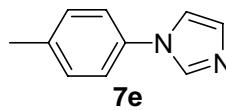
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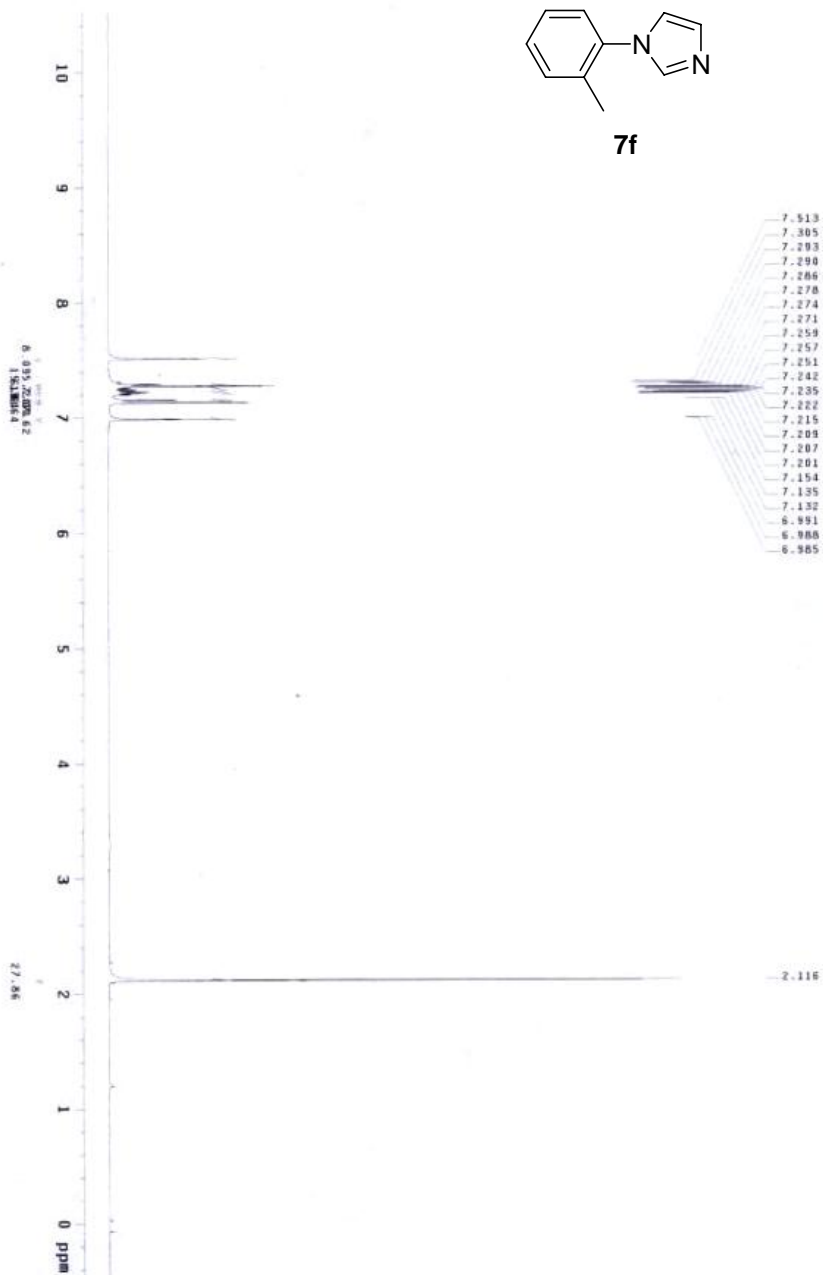
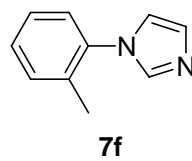
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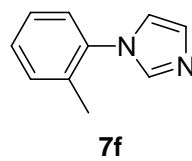
VJS-0666-22
Pulse Sequence: szpu1



MS436-CDCL3-H3-2008-12-27
Pulse Sequence: zgpg30



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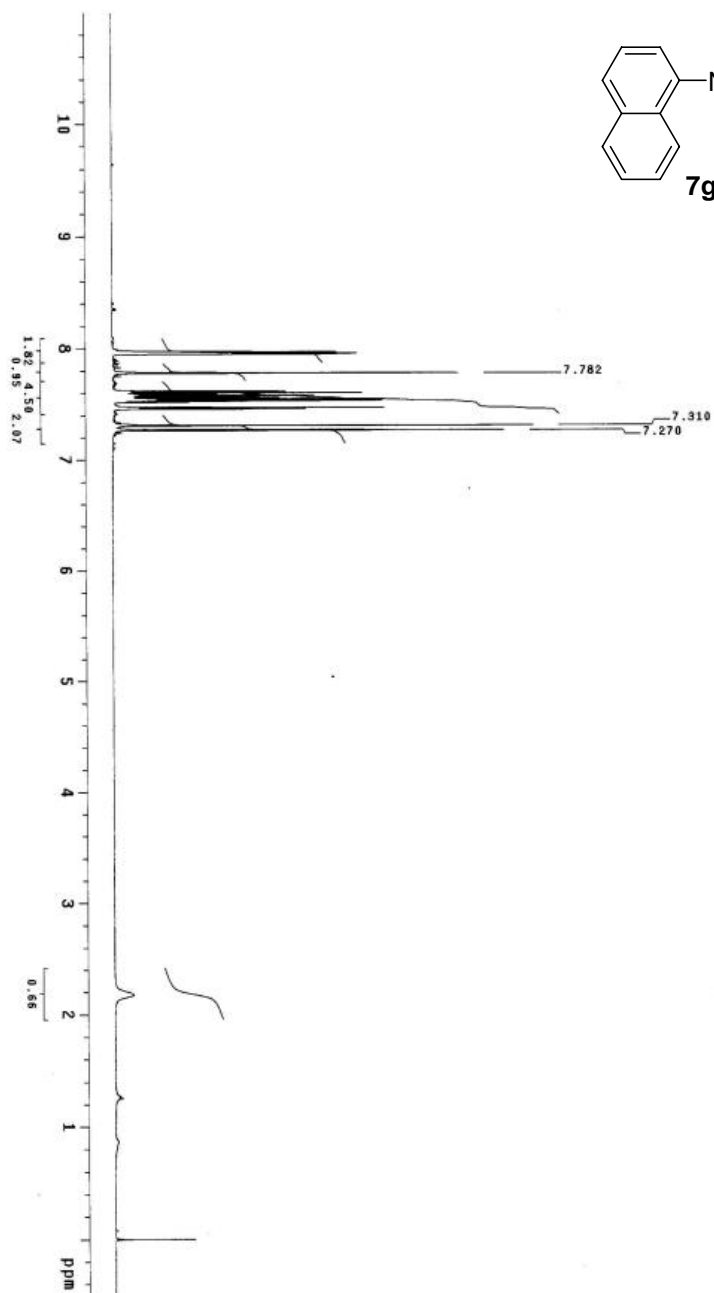
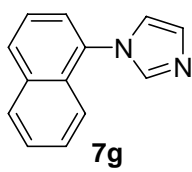
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77.326
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76.688

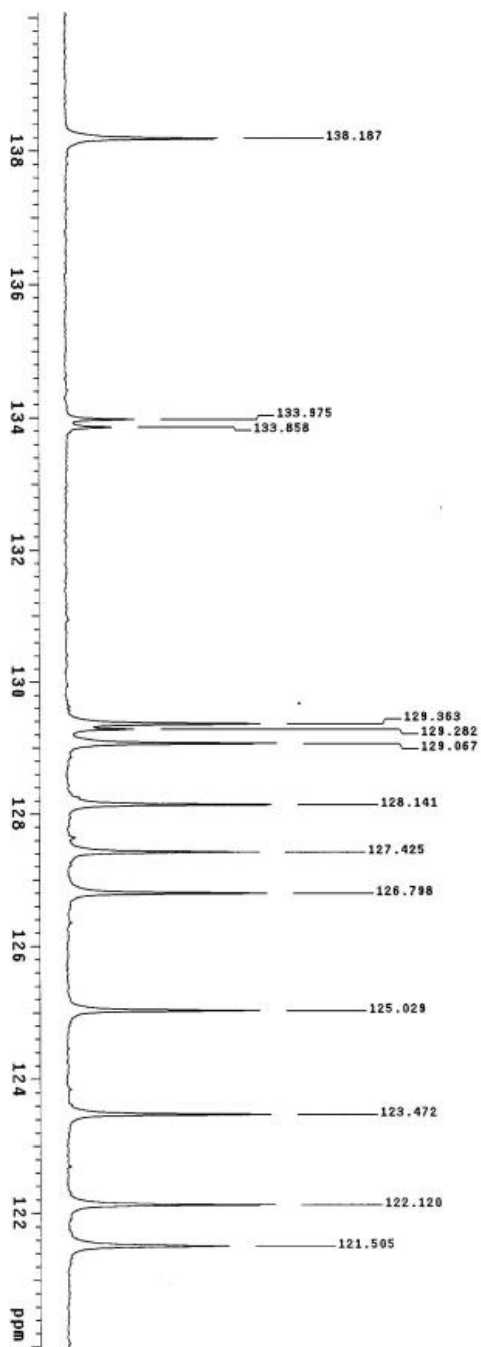
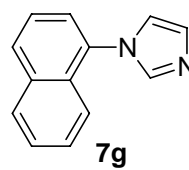
17.388

200 180 160 140 120 100 80 60 40 20 ppm

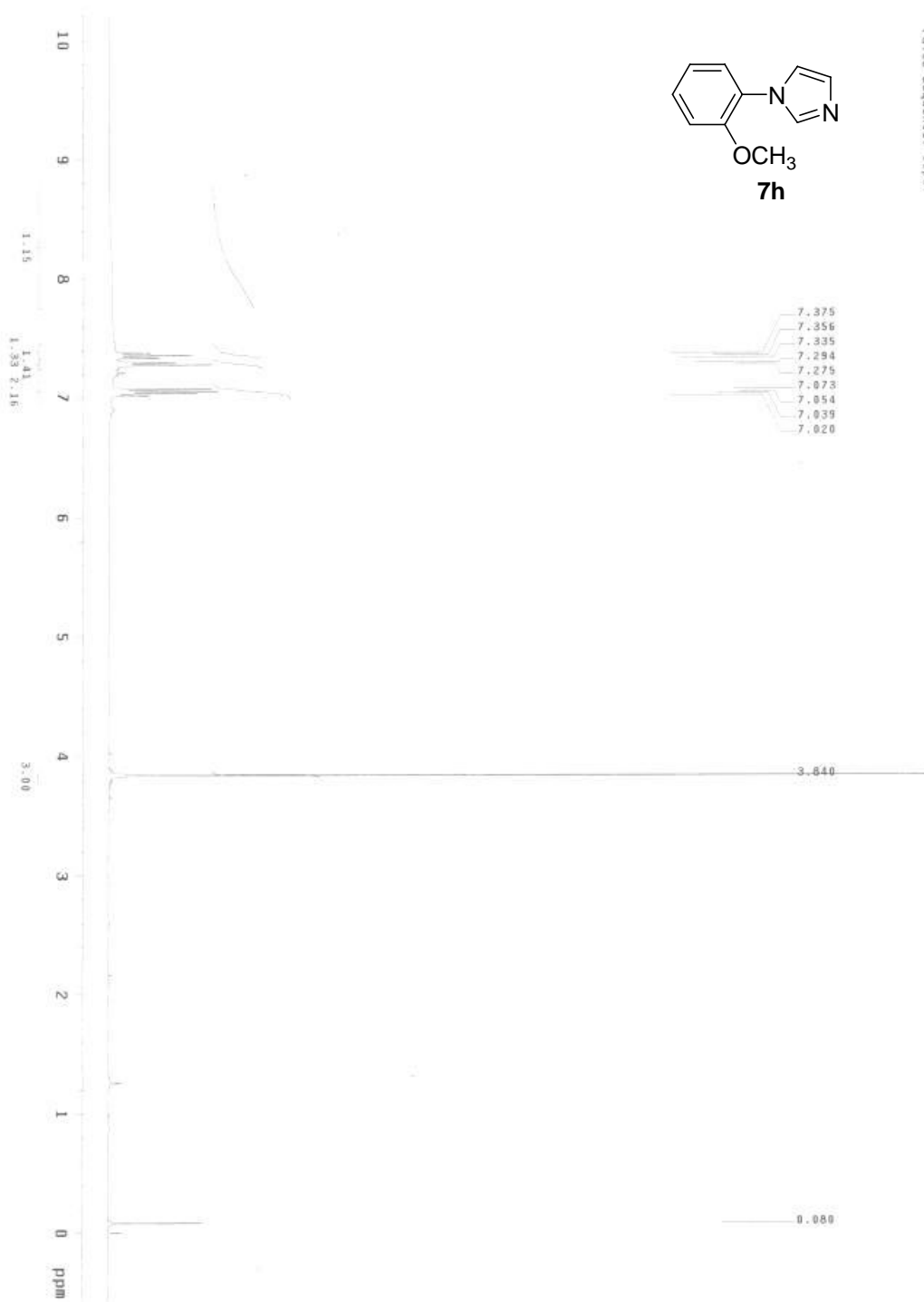
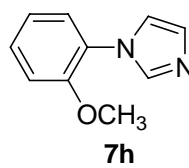
YJS-0606-11
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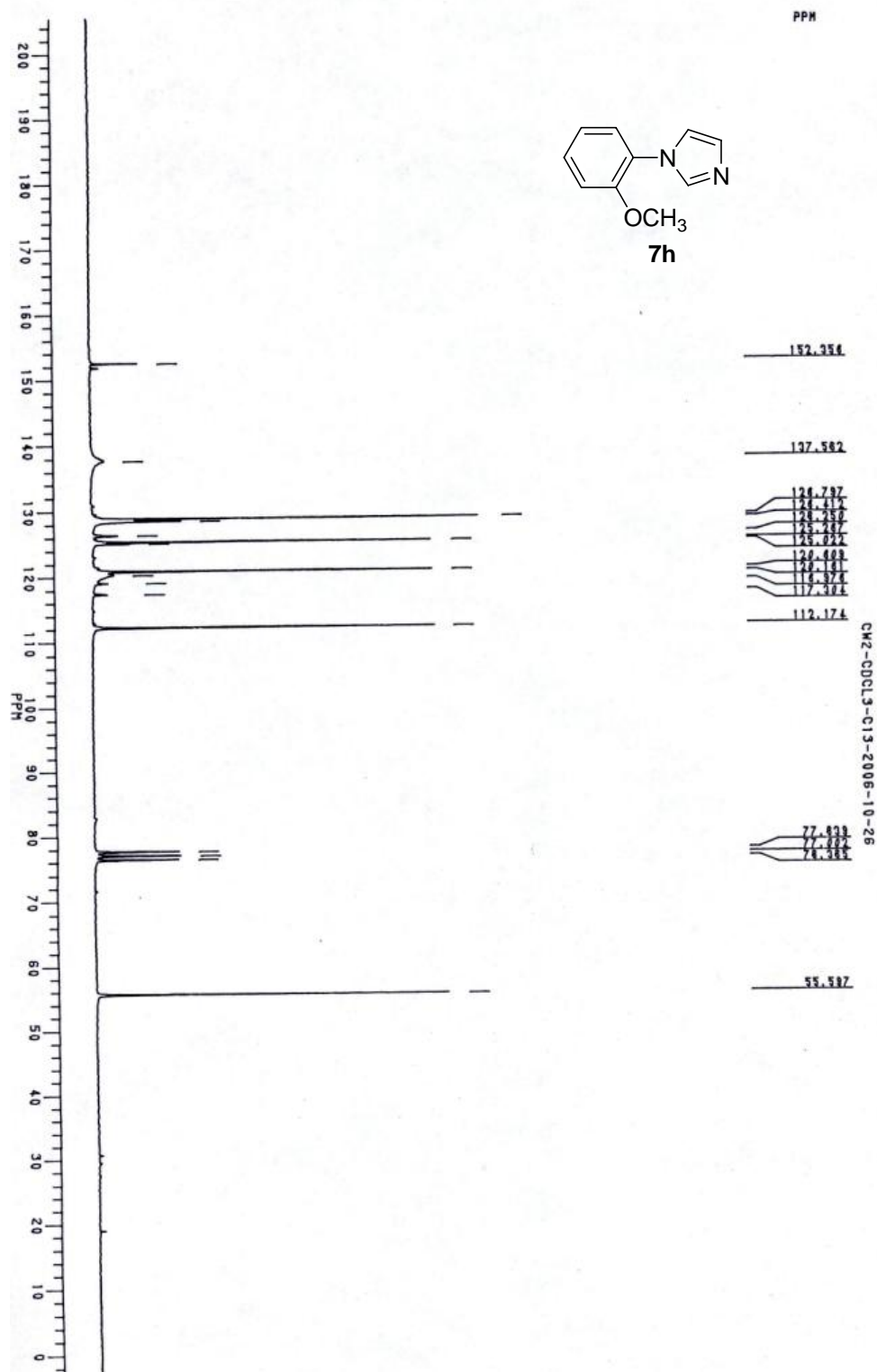


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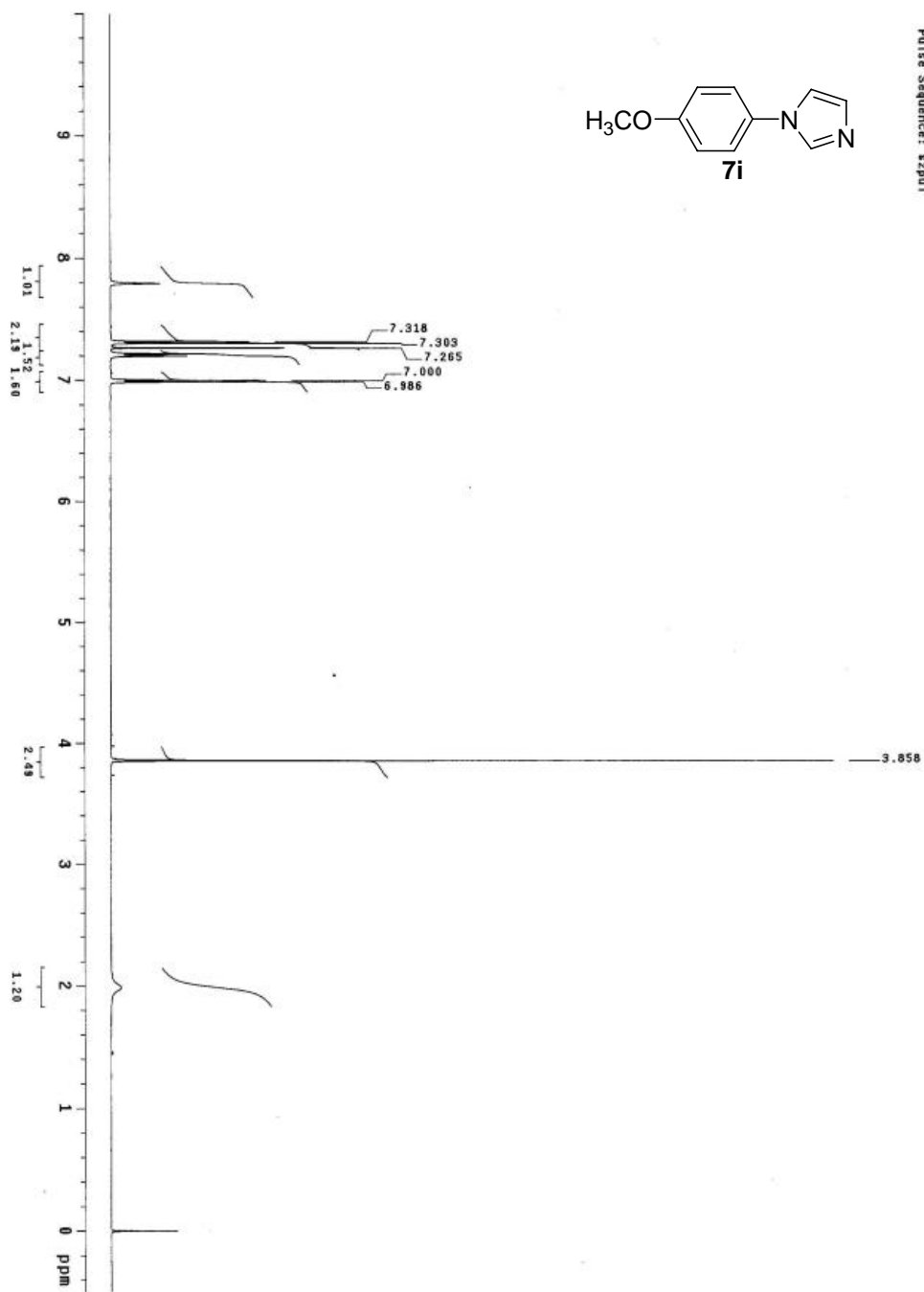
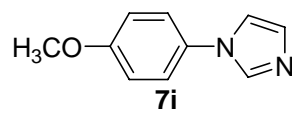


21837 M1 CDCl3 2006-9-14
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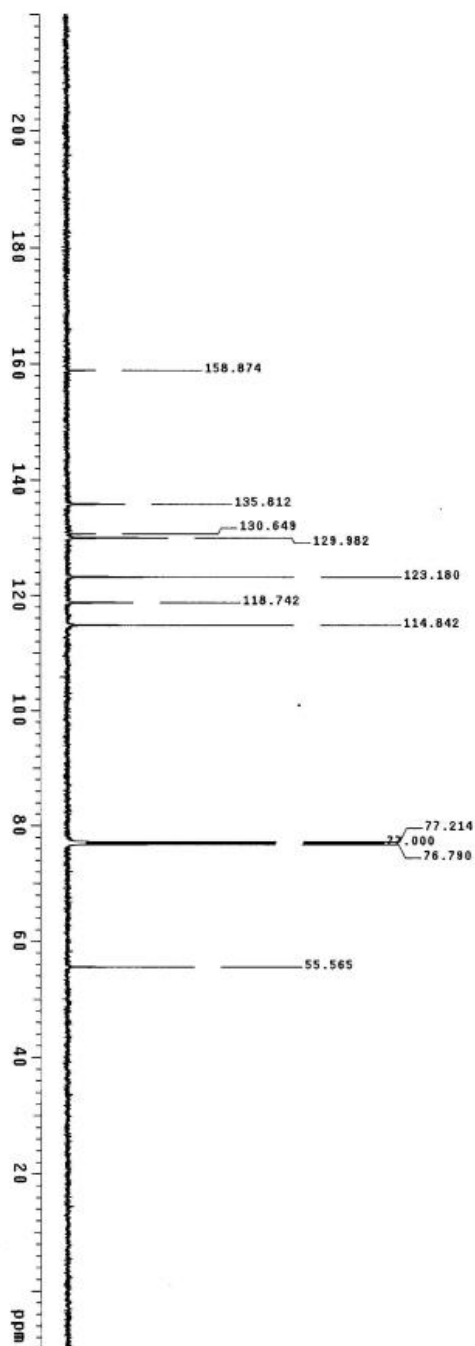
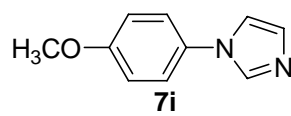




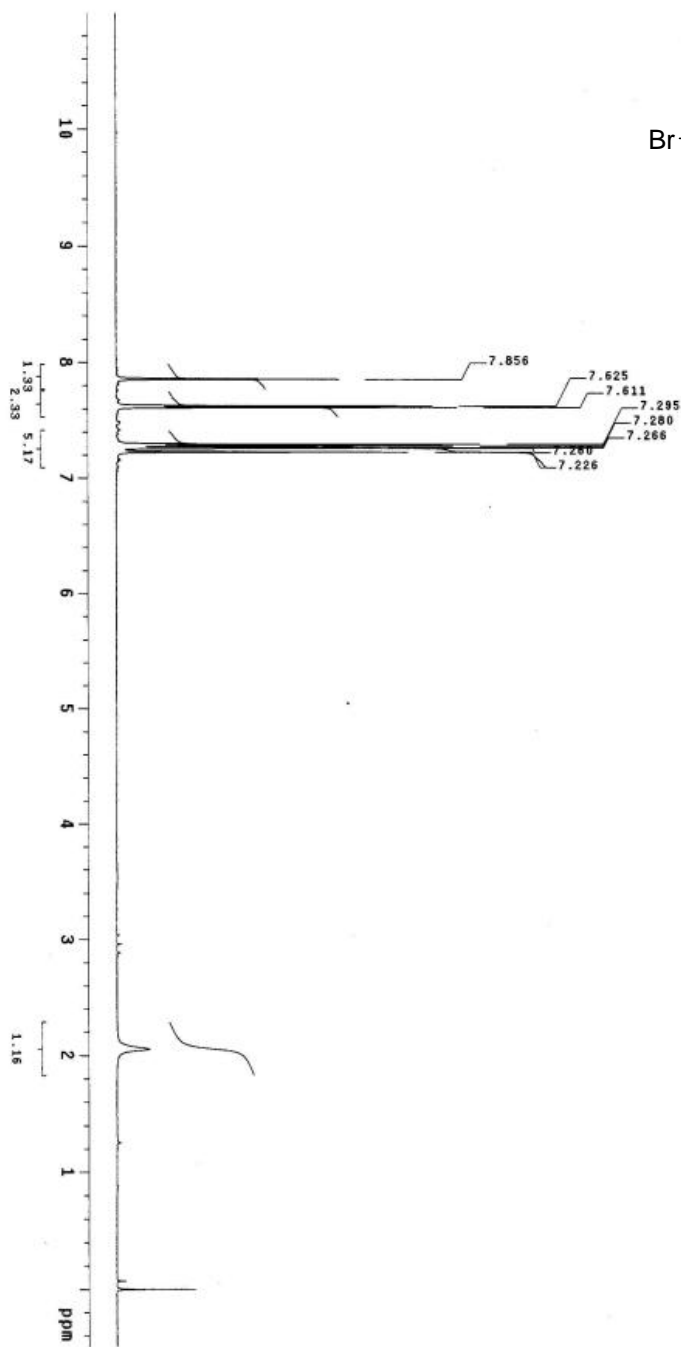
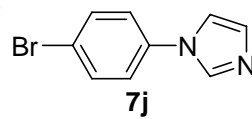
VJS-0606-15
Pulse Sequence: szpu1



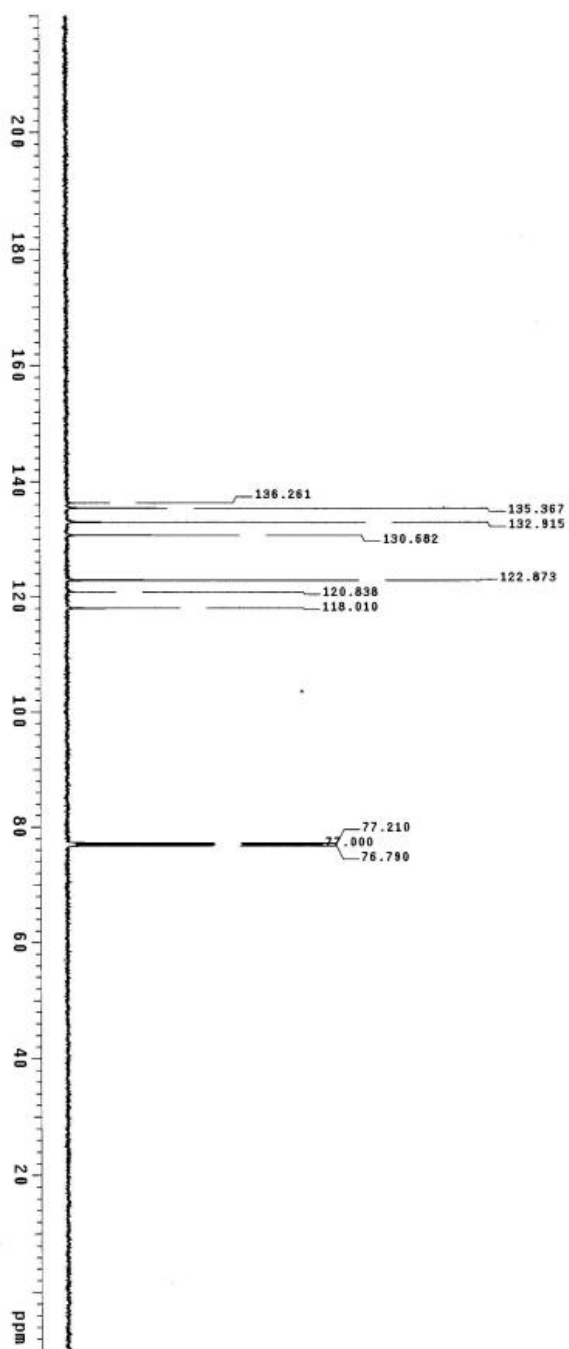
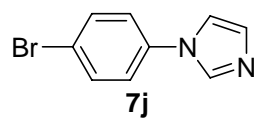
VJS-0608-15
Pulse Sequence: szput



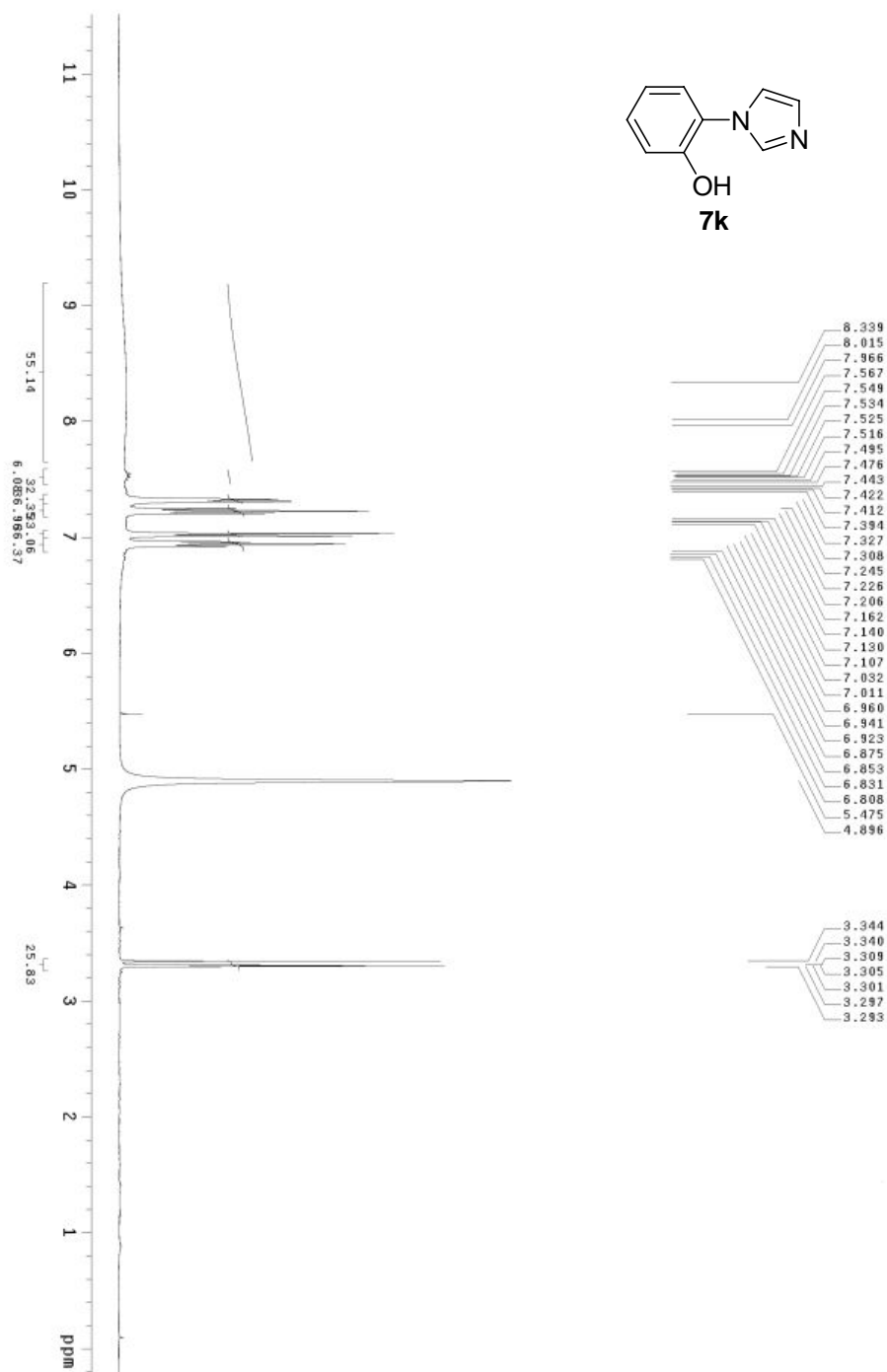
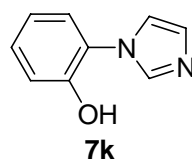
YJS-0808-16
Pulse Sequence: szpu1



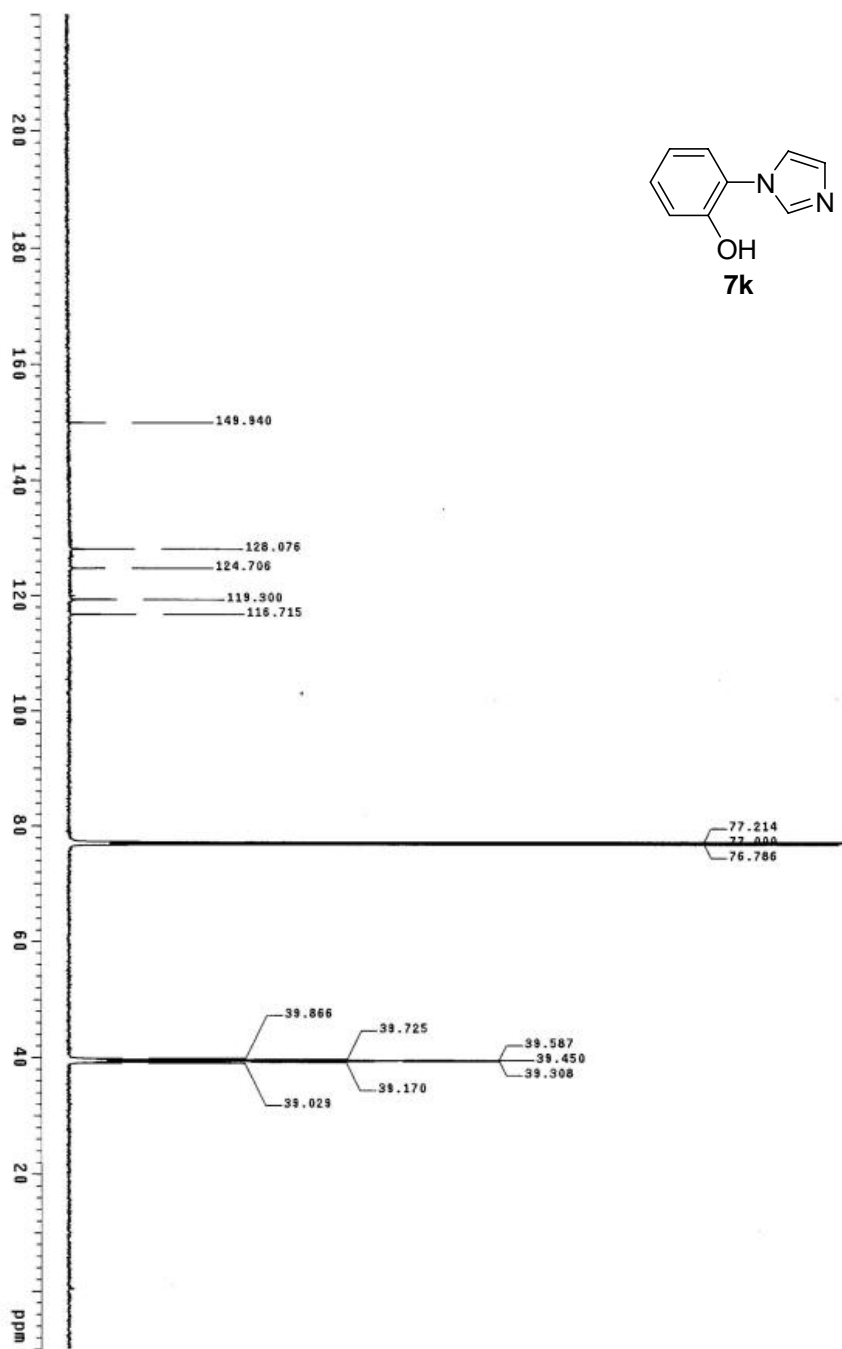
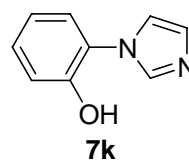
VJS-0606-16
Pulse Sequence: szpu1



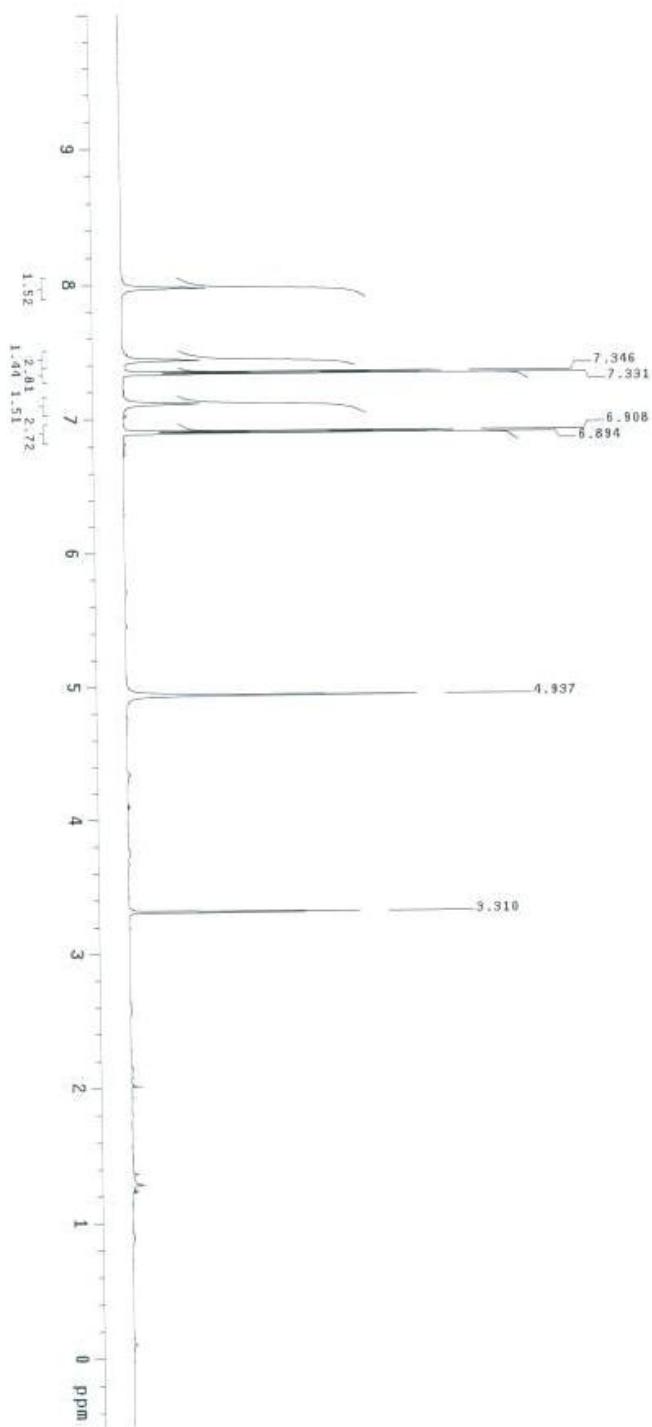
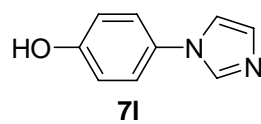
CM5-CD3OD-H1-2006-10-26
Pulse Sequence: szpul

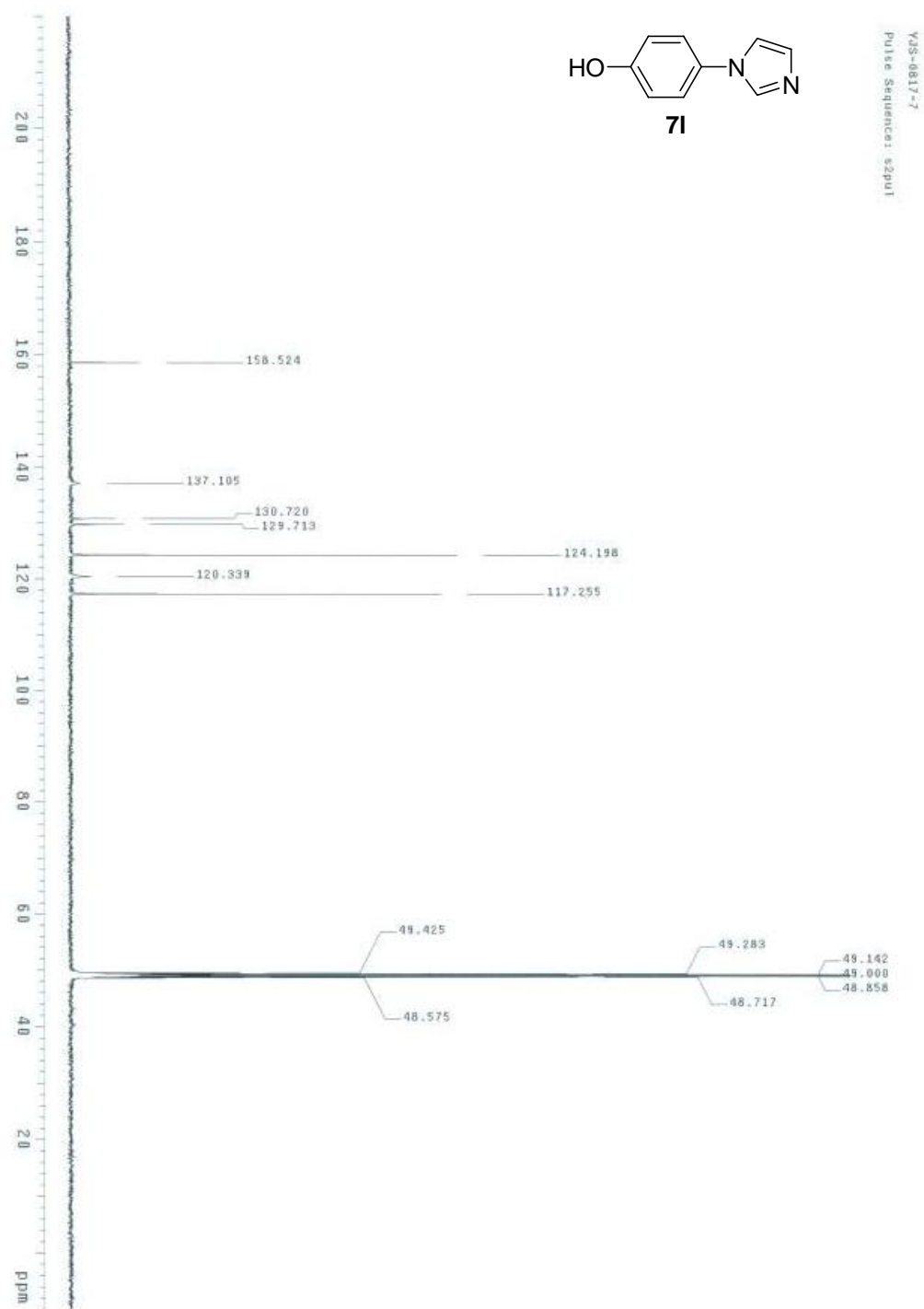


VJS-0806-23
Pulse Sequence: szpu1

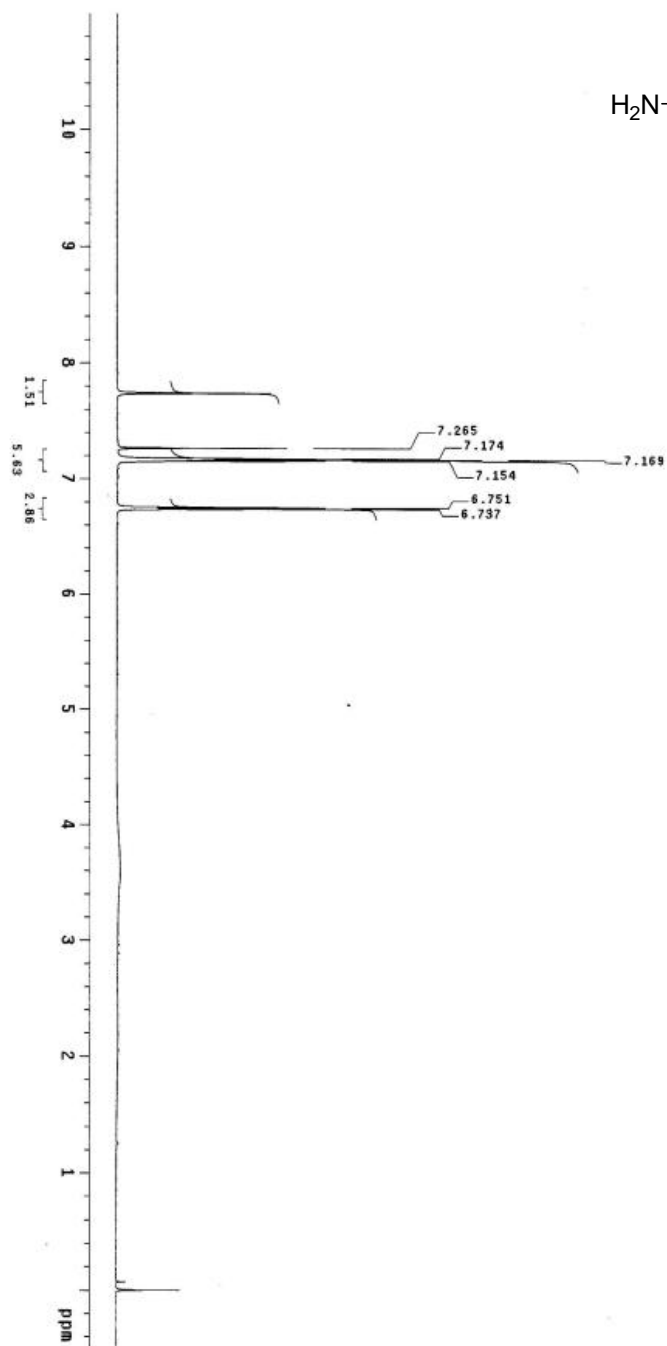
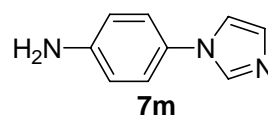


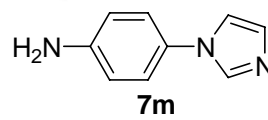
V05-0817-7
Pulse Sequence: zgpg30



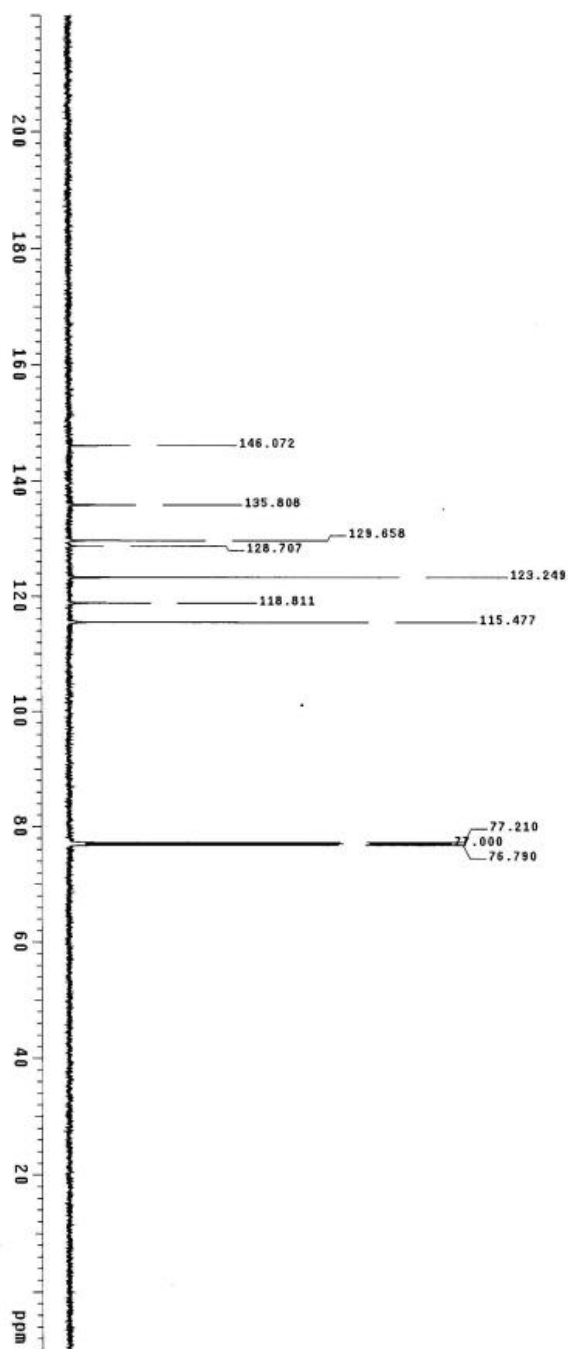


YJS-0606-14
Pulse Sequence: szpu1

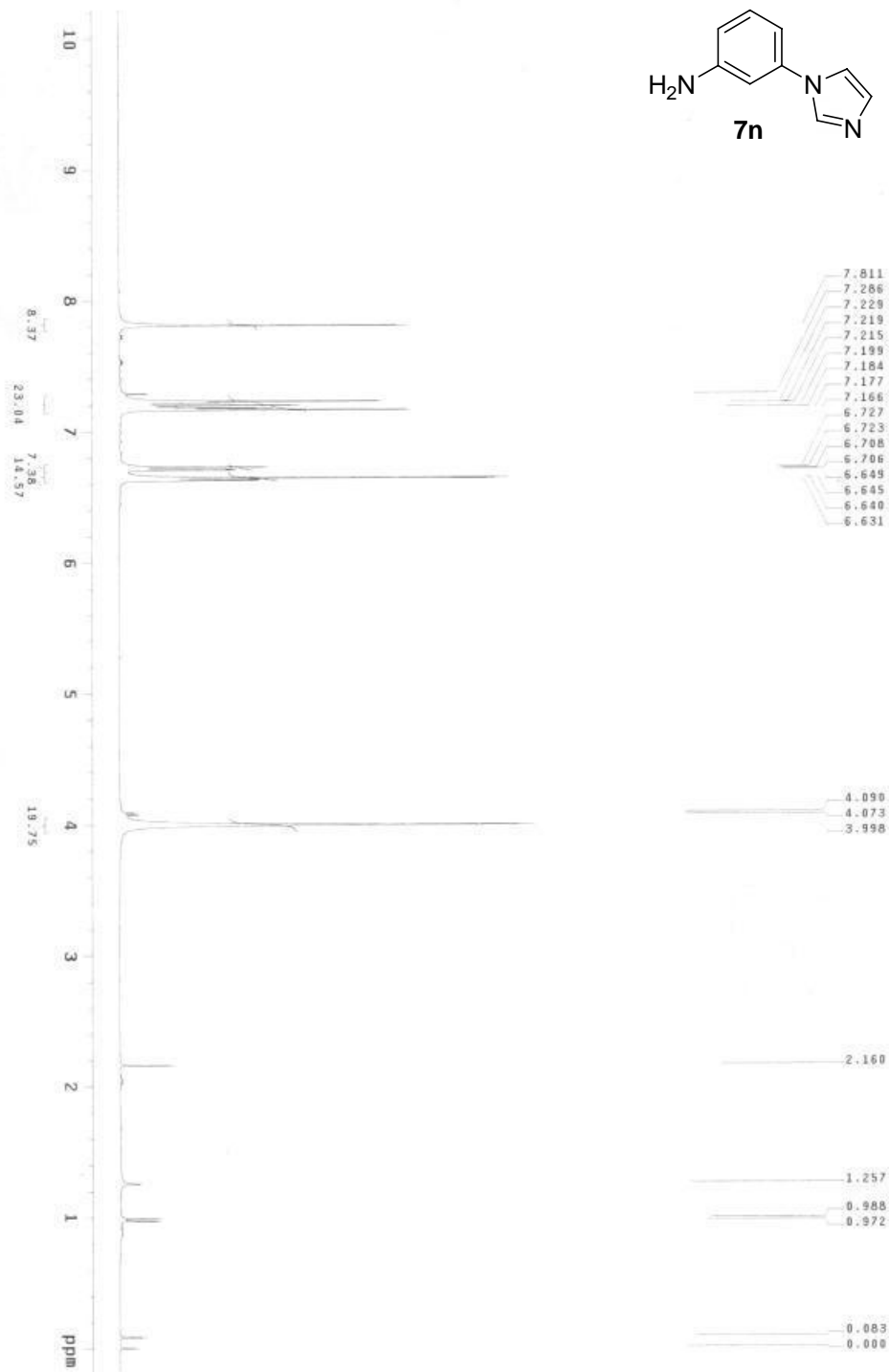
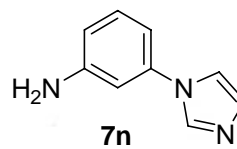


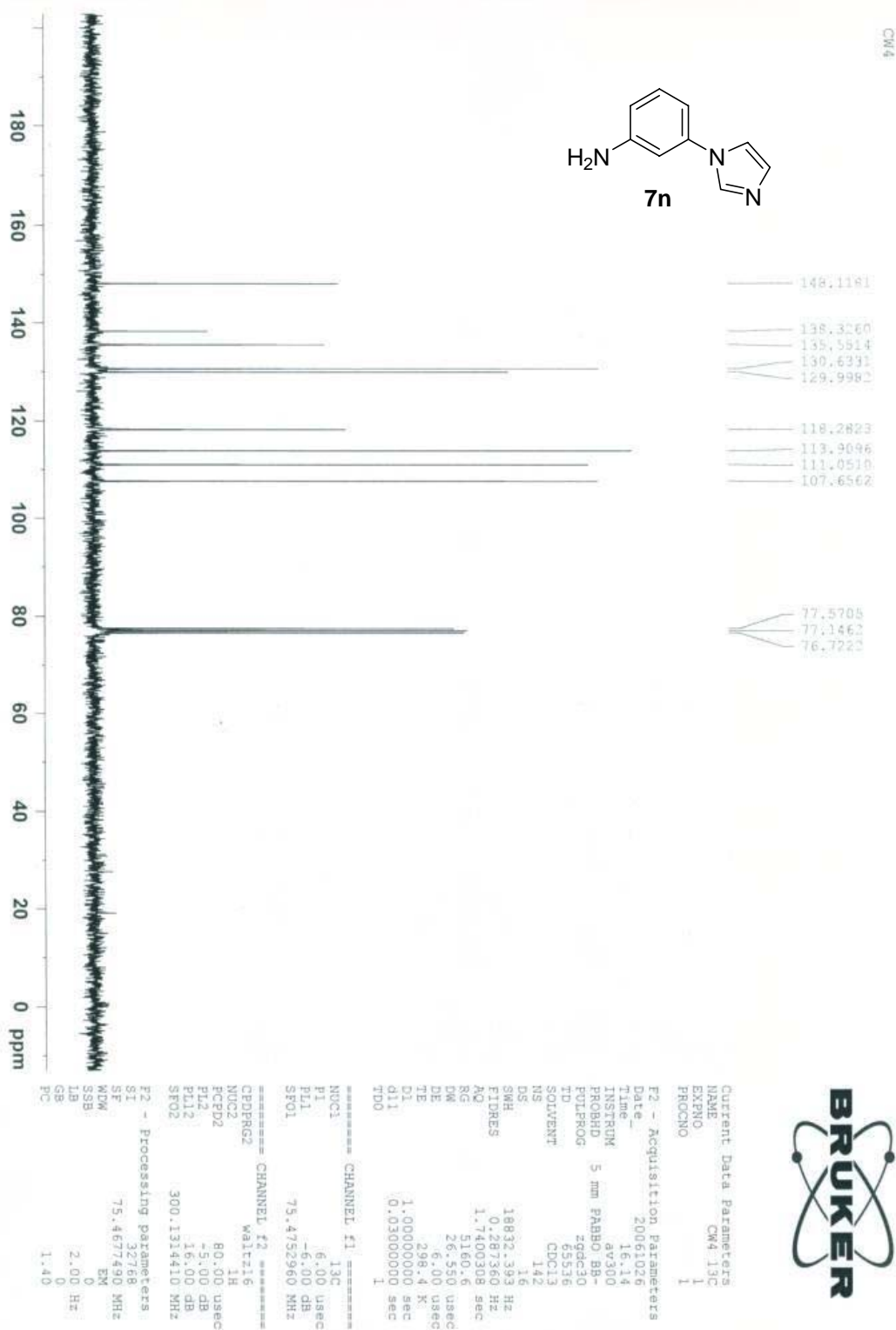
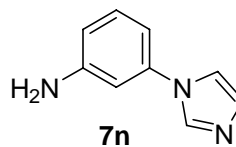


YJS-0606-14
Pulse Sequence: szput

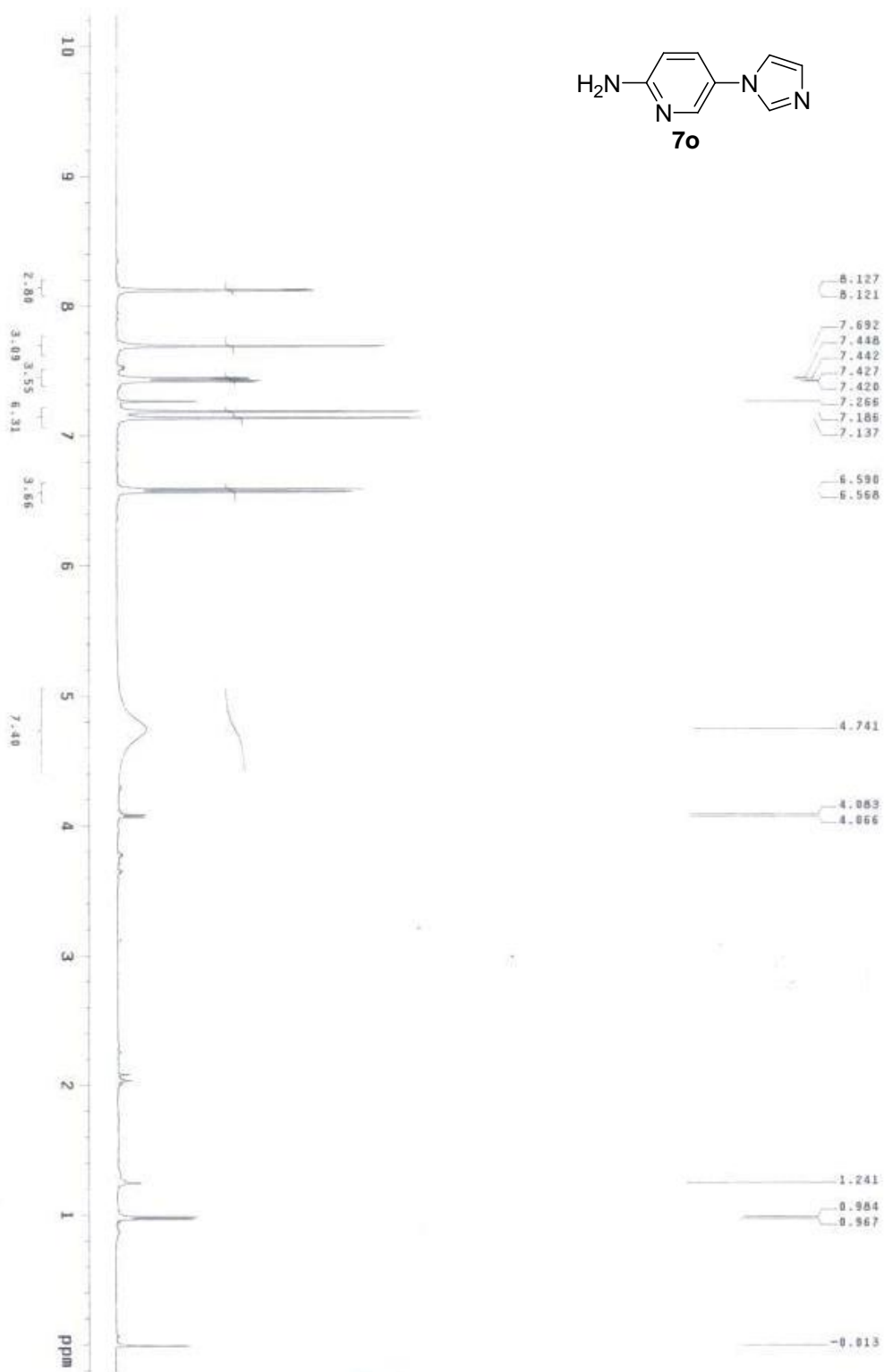
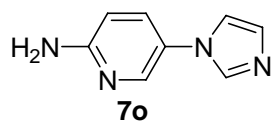


C44 H1 CQC13 2006-10-26
Pulse Sequence: szpul

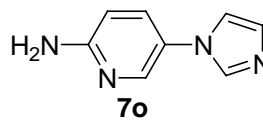




245--4-CDCl3-H1-2006-10-25
Pulse Sequence: szpu1



MS(ESI)-C004-3-CL3-2007-1-3
 File Sequence: 82933



180
160
140
120
100
80
60
40
20
ppm

158.235

142.879

137.511

130.263

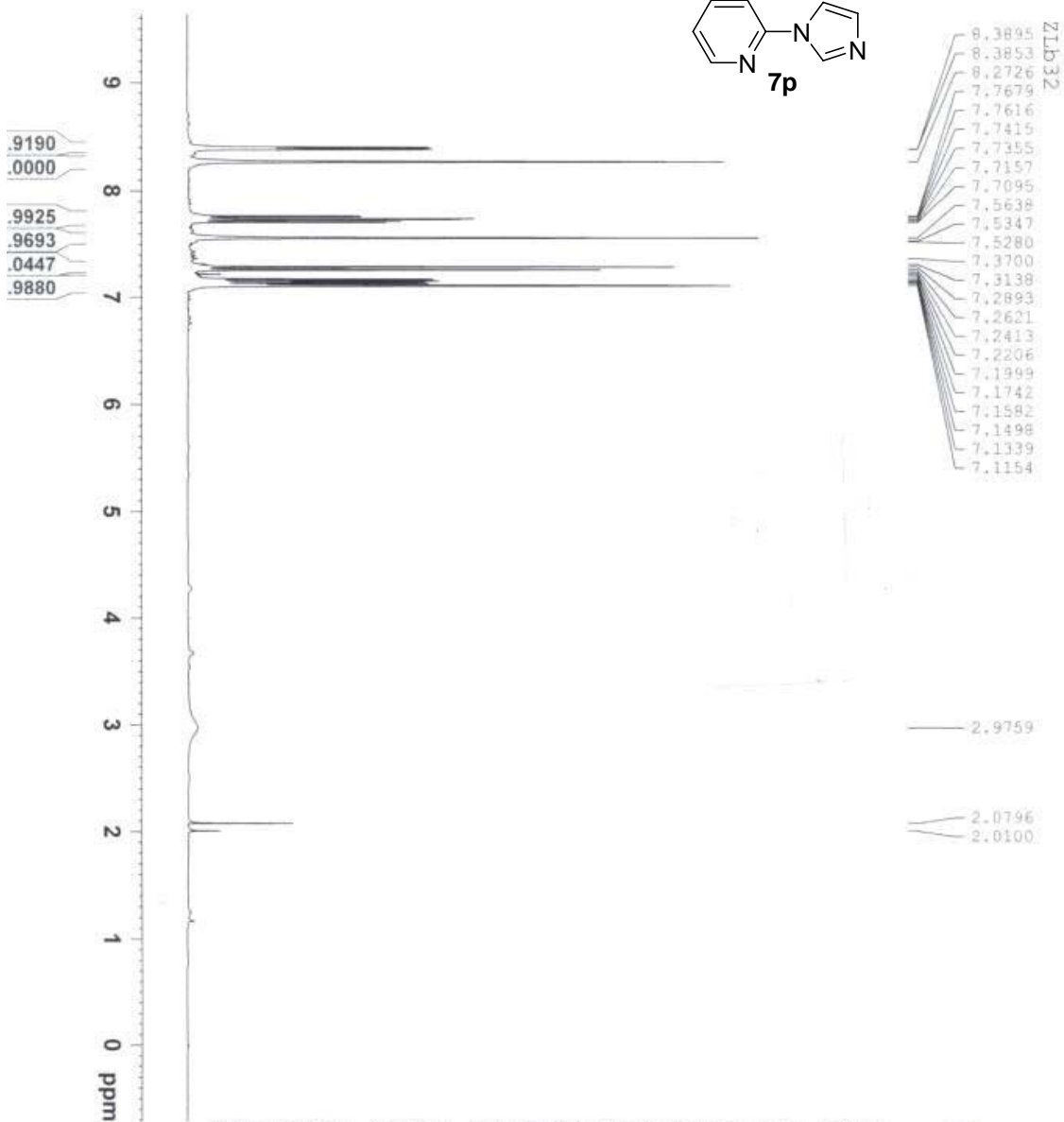
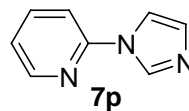
125.734

108.718

77.487

77.176

76.885



Current Data Parameters
NAME 21b32
EXPNO 1
PROCNO 1

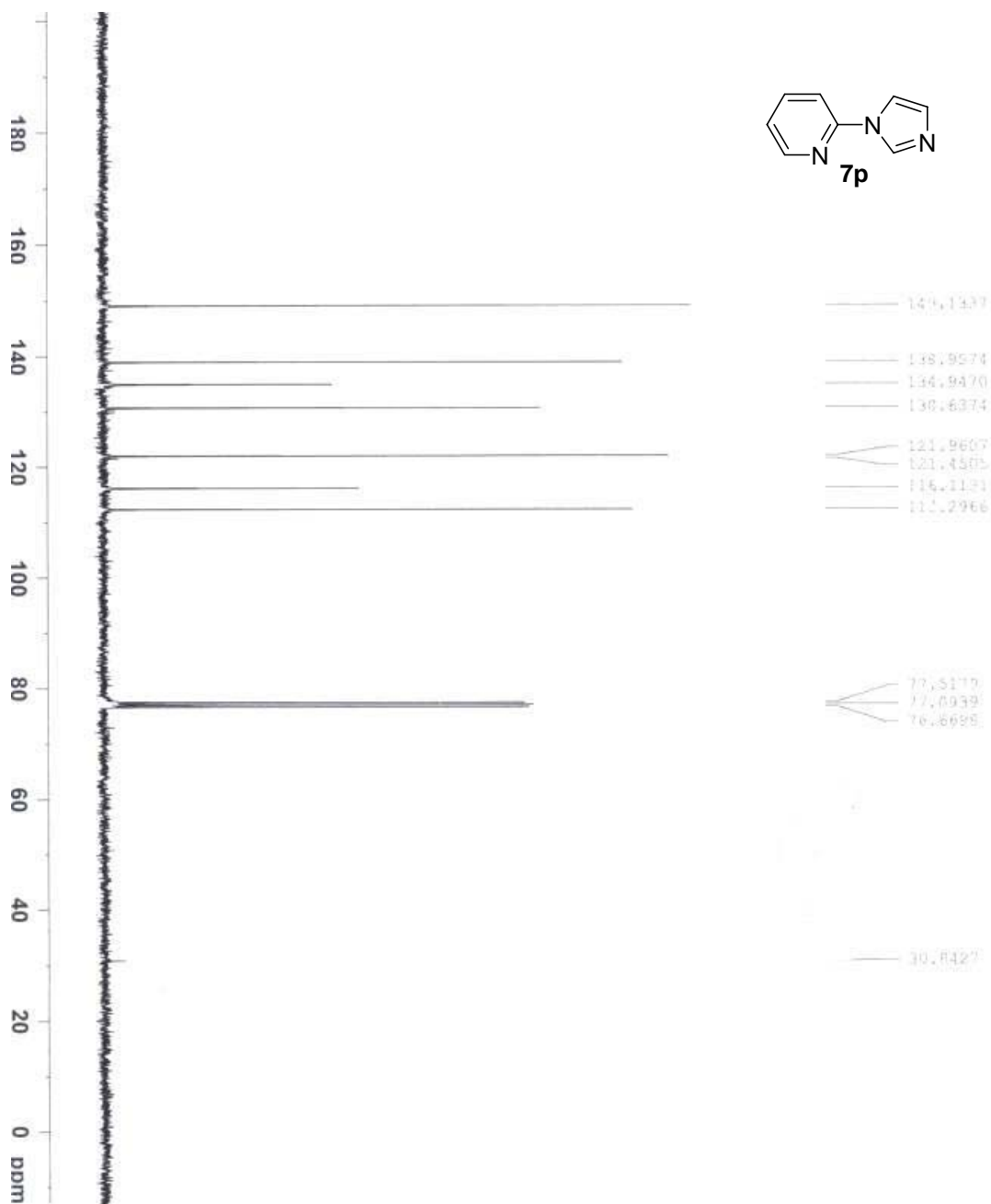
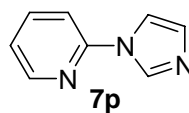
F2 - Acquisition Parameters

Date_ 20060803
Time 11.24
INSTRUM av300
PROBHD 5 mm F4BBO BB-
PULPROG zg30
TD 32768
FIDRES 0.182959 Hz
SOLVENT CDCl3
NS 8
DS 4
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
RG 83.400 usec
DE 6.00 usec
TE 297.7 K
D1 2.50000000 sec
TD0 1

CHANNEL f1 1H
NUC1 1H
P1 7.70 usec
PL1 -5.00 dB
SFO1 300.1324010 MHz

F2 - Processing parameters
SI 16384
SF 300.1300211 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

ZLB32 13C



149.1437
138.9574
134.9470
130.6374
121.9607
121.4585
116.1131
111.2966

77.5179
77.0939
76.6695



Current Data Parameters
NAME ZLB32 13C
EXPNO 1
PROCNO 1

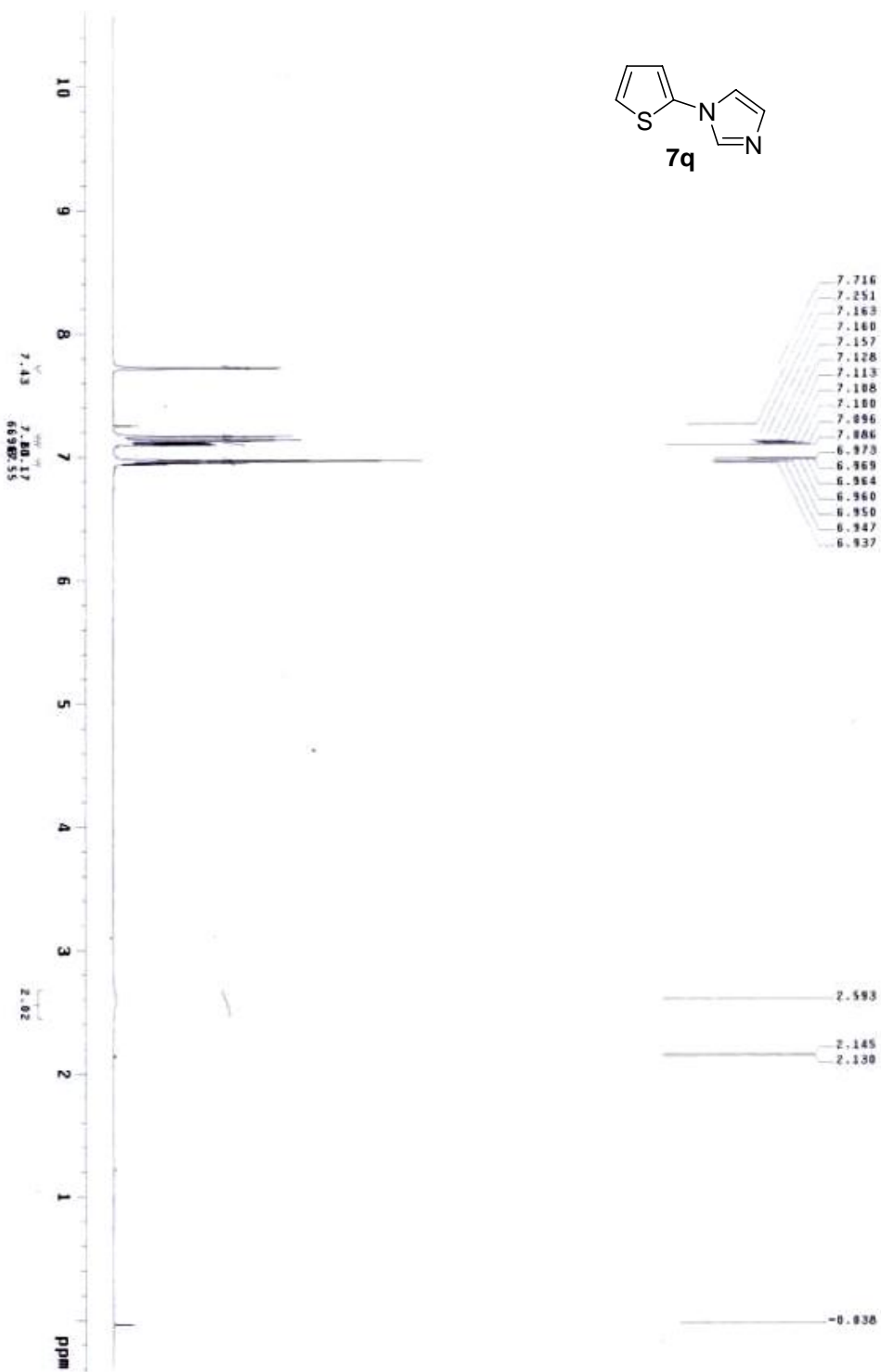
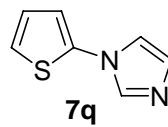
F2 - Acquisition Parameters
Date_ 20060803
Time 16.02
INSTRUM av300
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 551
DS 16
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 11588.2
RG 26.550 usec
DE 6.00 usec
TE 299.7 K
D1 1.00000000 sec
d11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz

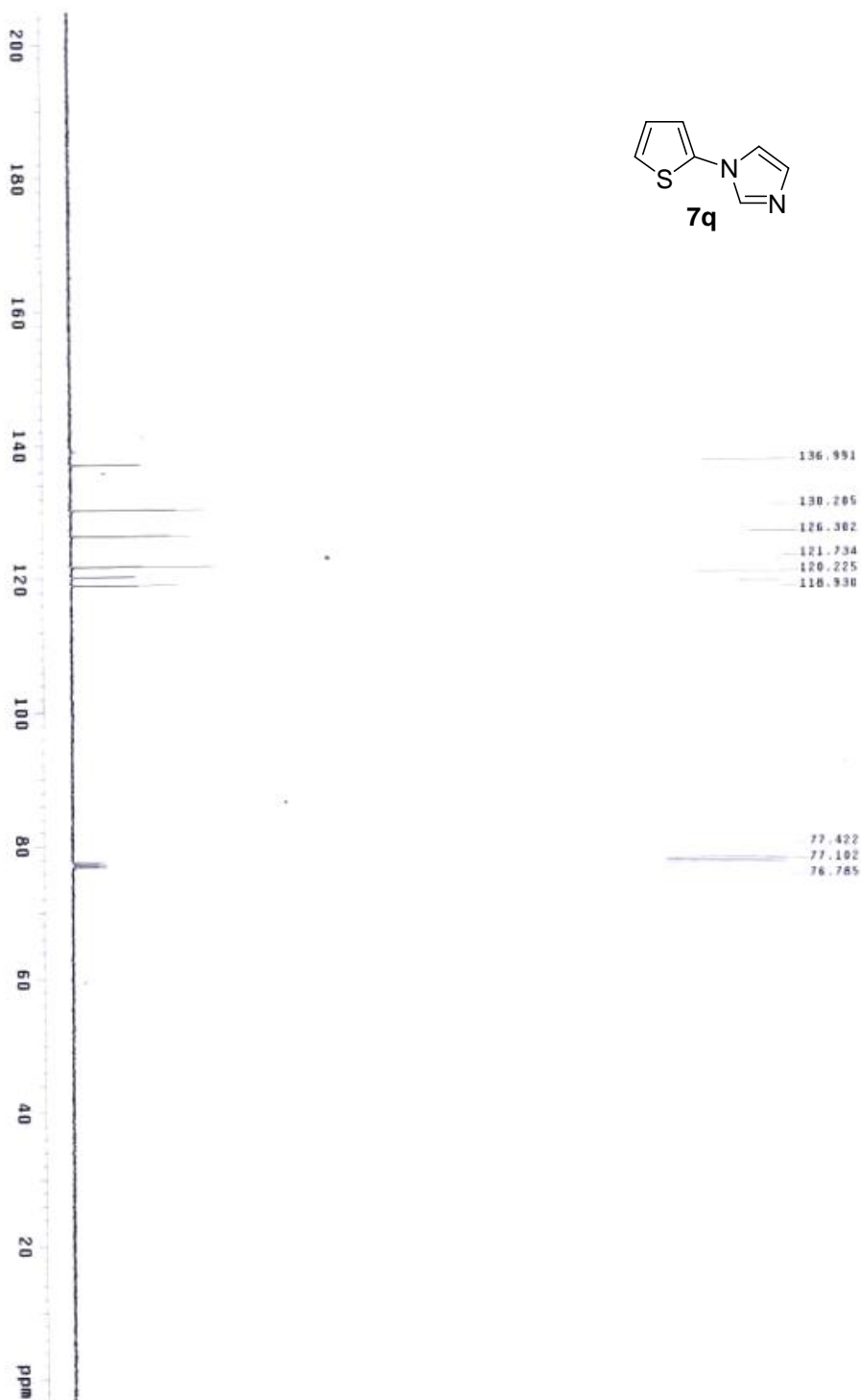
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz

F2 - Processing parameters
SI 32768
SF 75.467490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

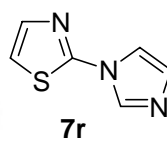
MSA37-CDCl₃-H₂-2006-12-22
Pulse Sequence: zgpg30



MS437-CDCL3-Cl3-2006-12-31
Pulse Sequence: zgpg30



MS188-CDCL3-H1-2006-12-30
Pulse Sequence: zgpg1

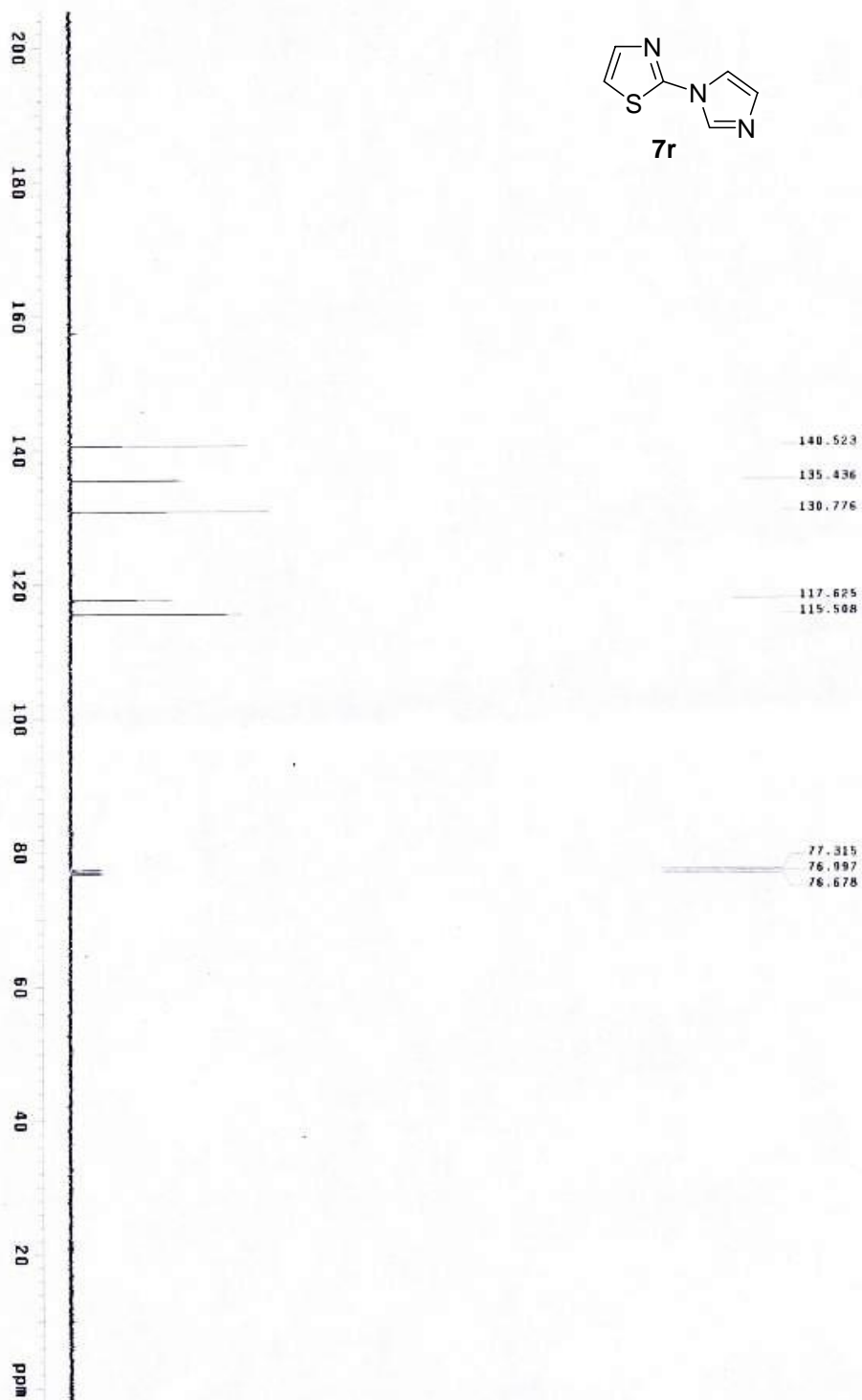
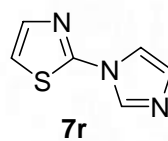


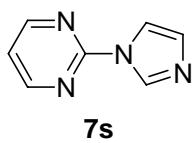
2.571

-0.045

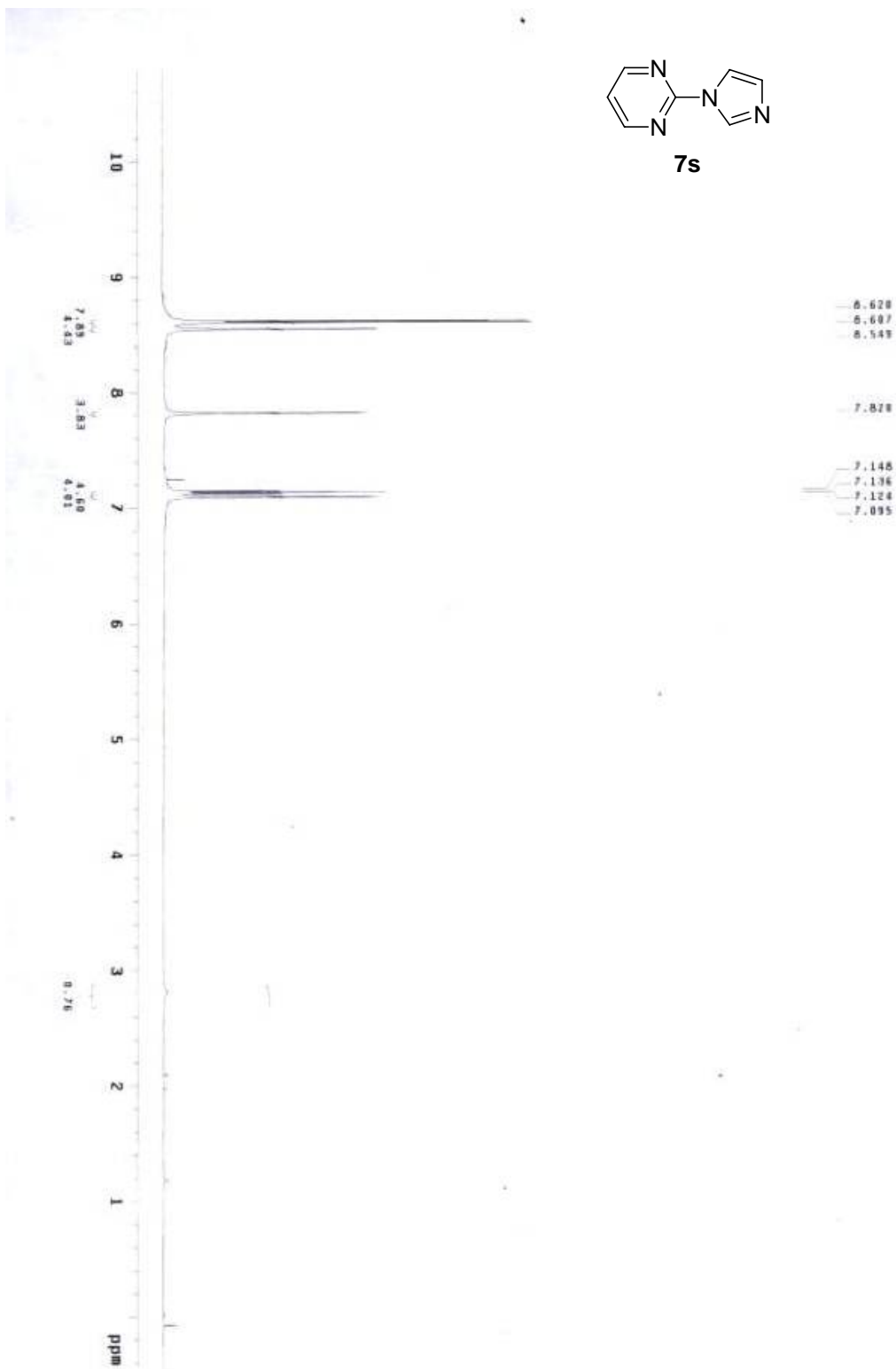


MS198-CDCl₃-3-C13-2007-1-4
Pulse Sequence: zgpg30

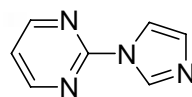




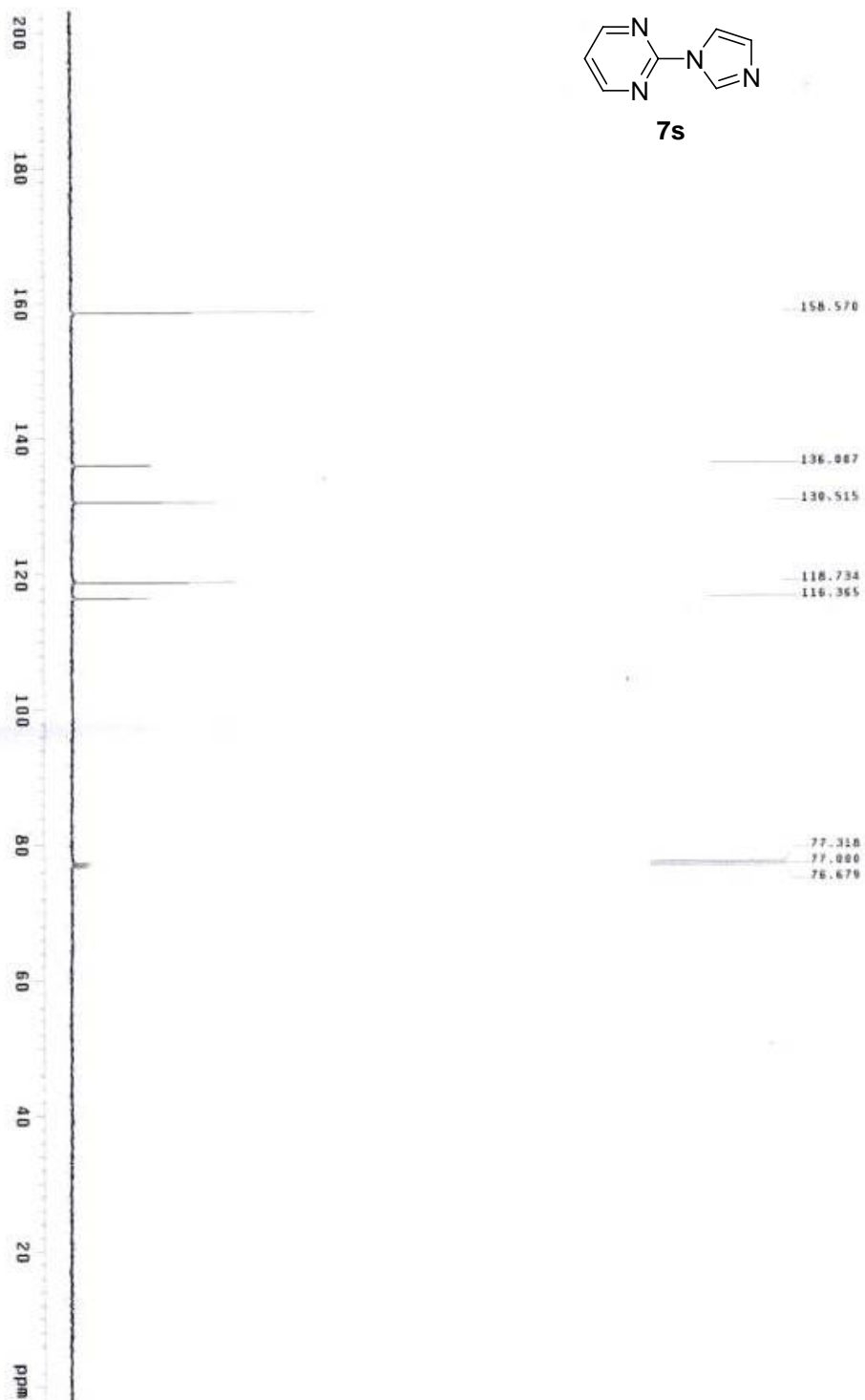
MS491-CDCl₃-H₂-2086-12-27
 Pulse Sequence: zgpg30



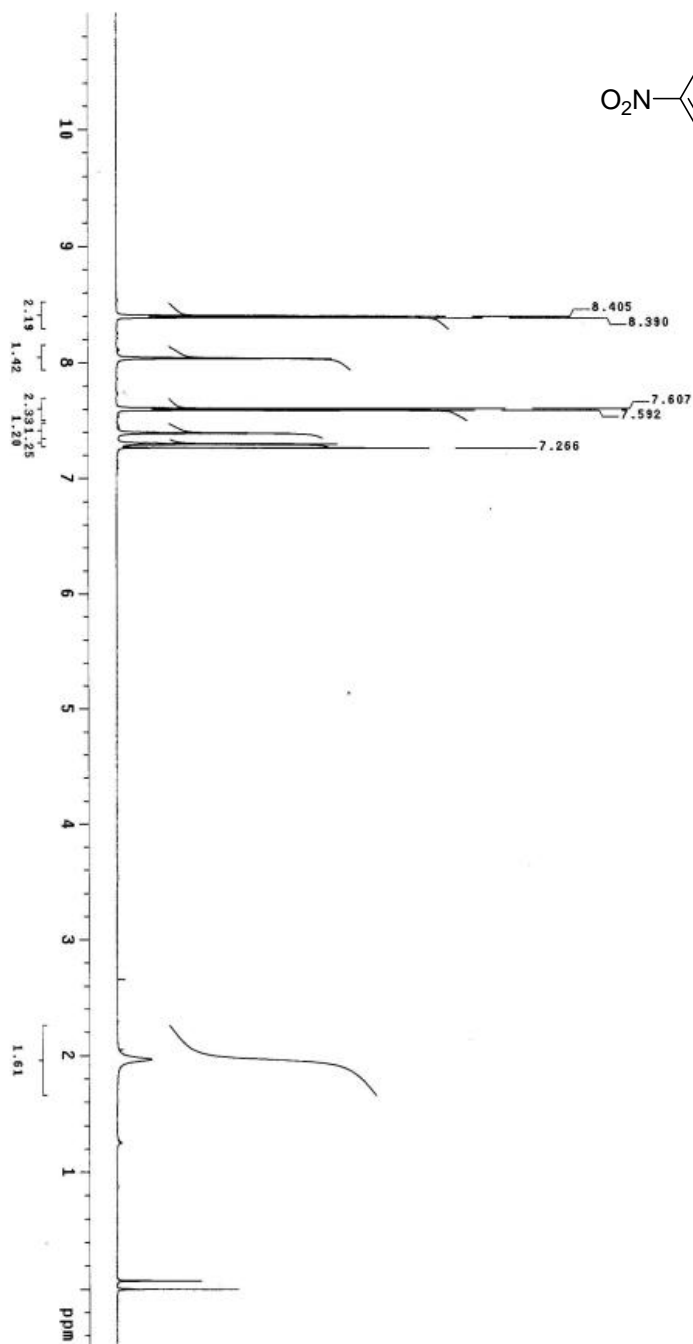
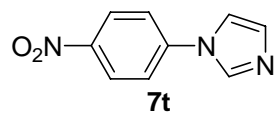
MS194-CDCl₃-C13-200K-12-10
Pulse Sequence: zgpg30



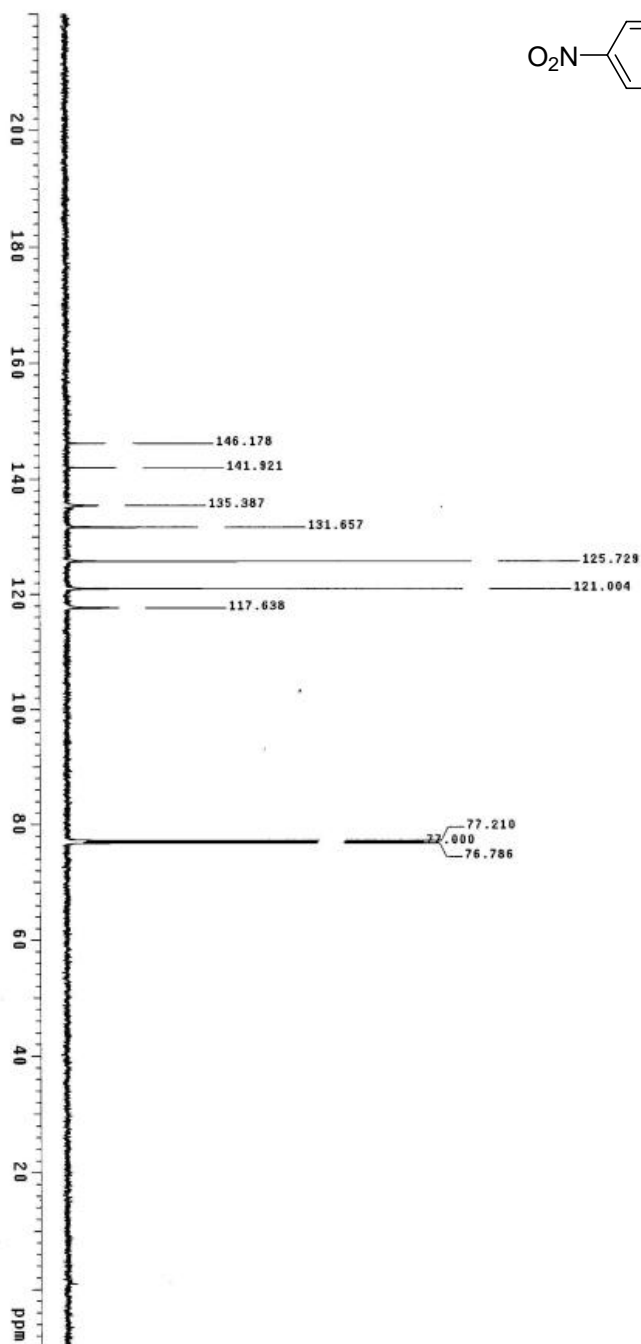
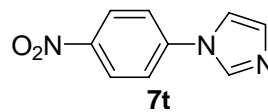
7s



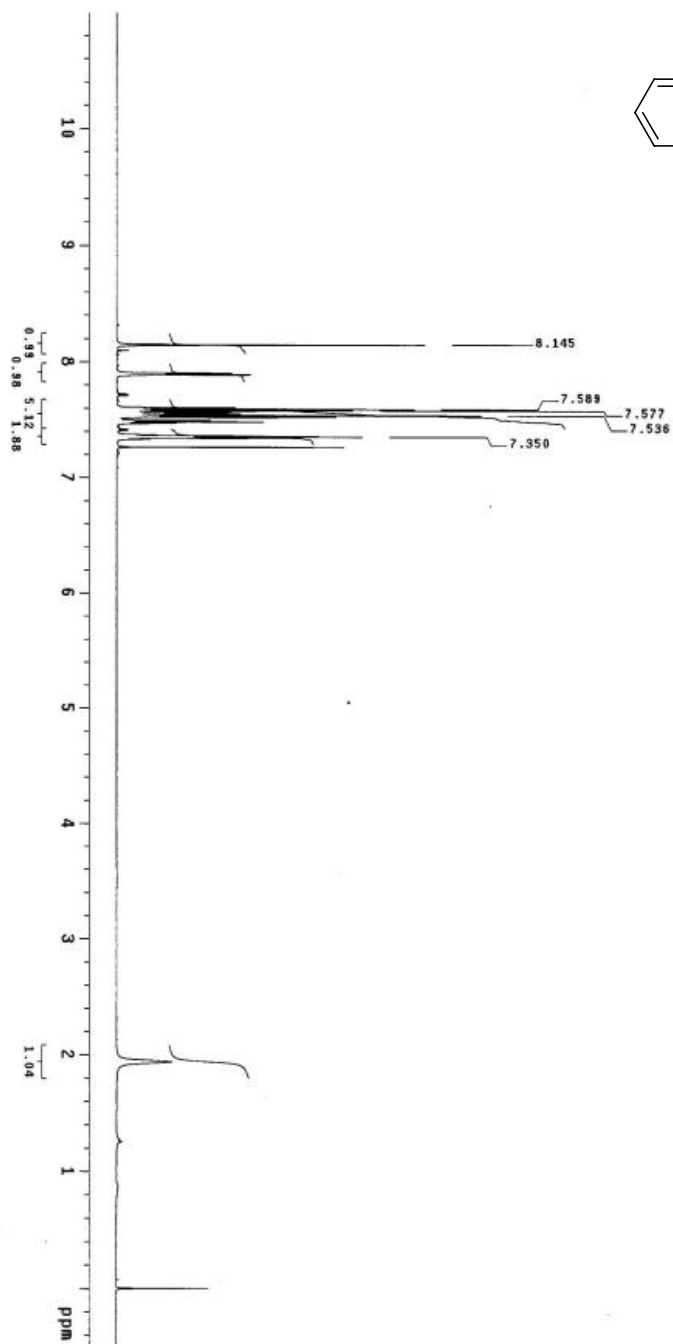
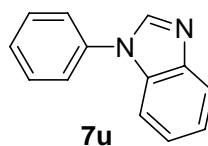
VJS-0606-18
Pulse Sequence: szpu1



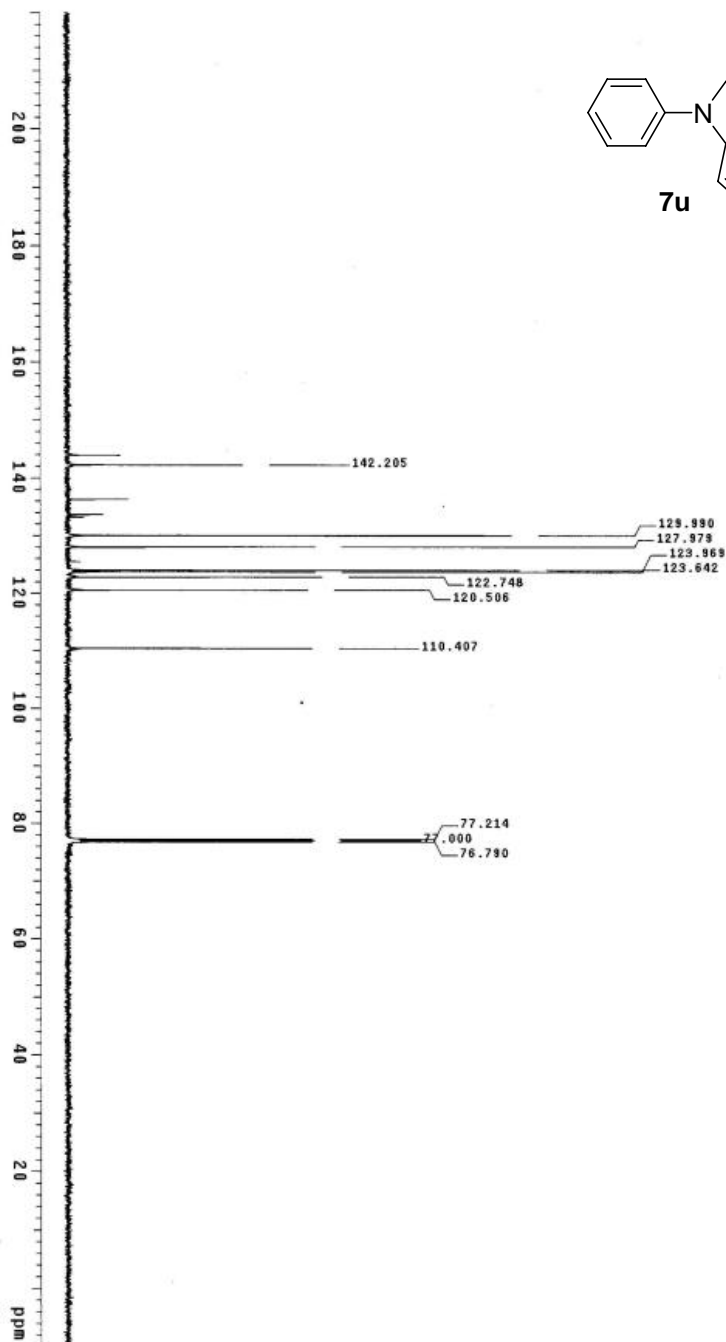
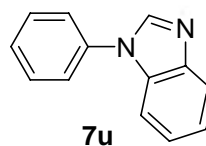
YJS-0606-18
Pulse Sequence: szpu1



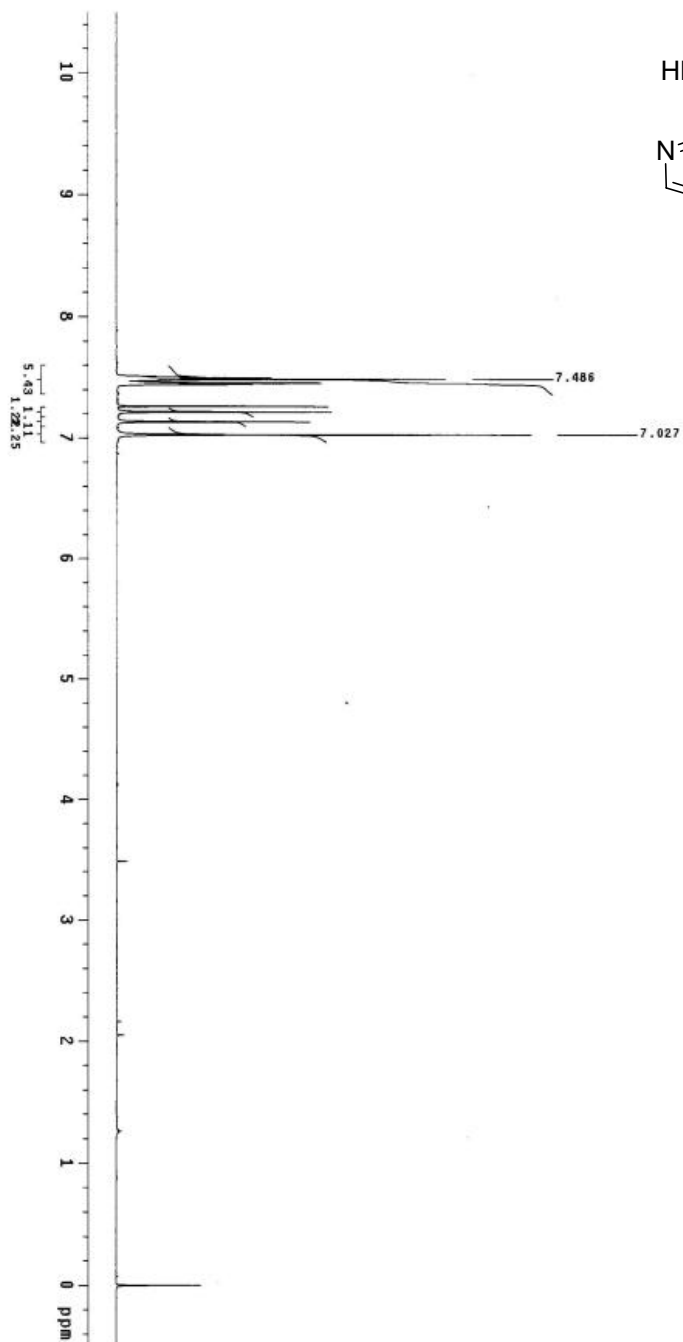
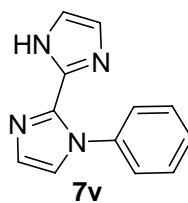
VJS-0606-13
Pulse Sequence: zgpg30



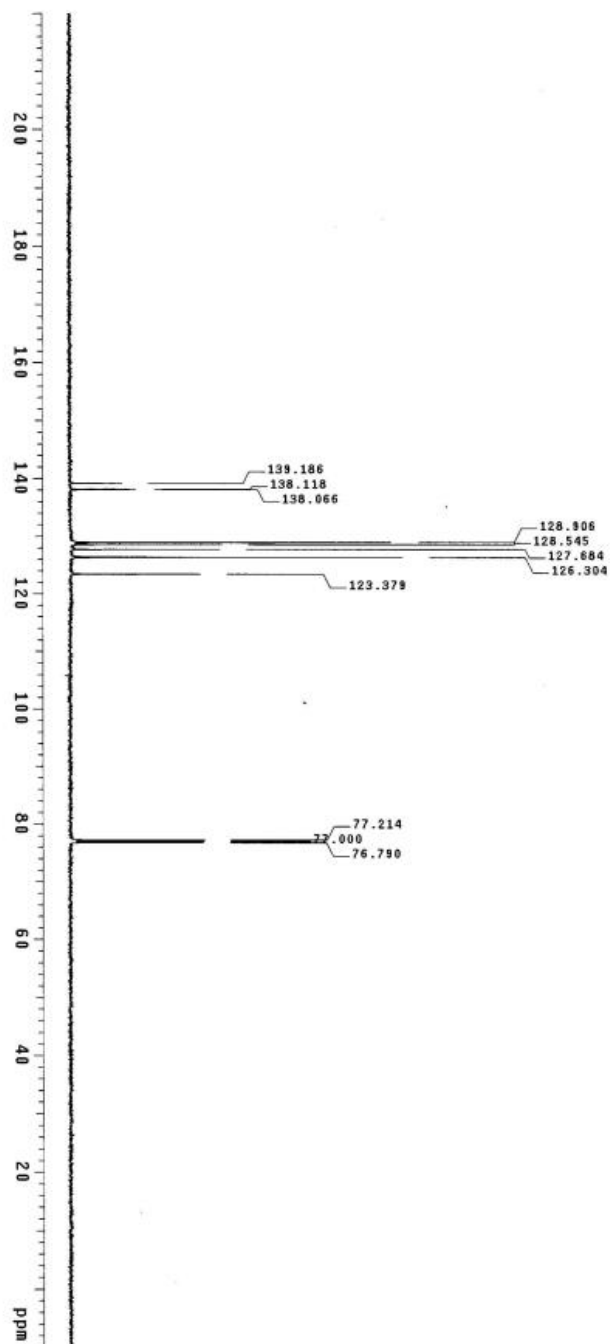
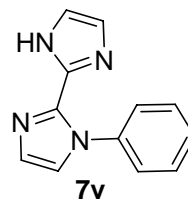
YJS-0606-13
Pulse Sequence: szpu1



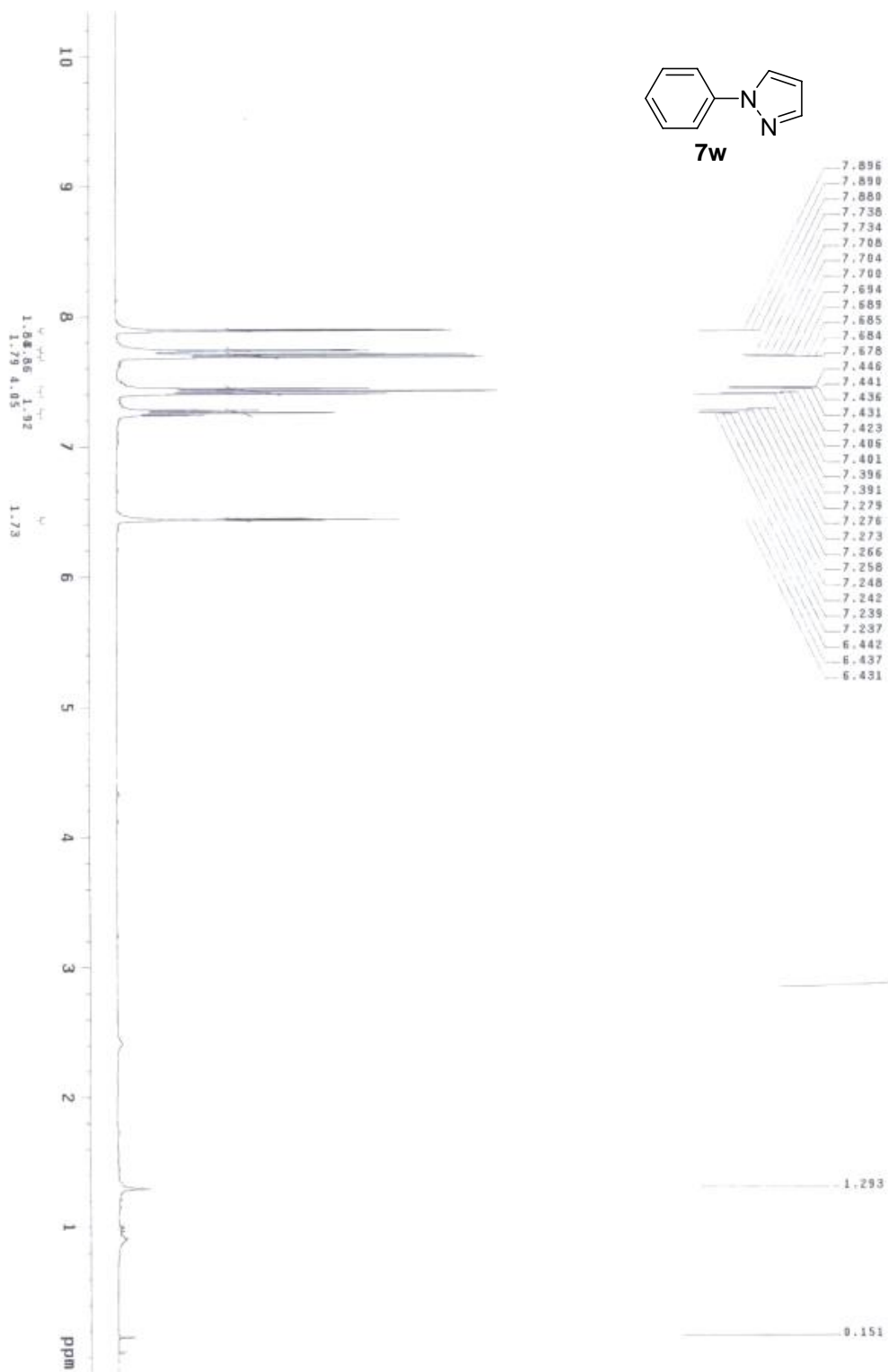
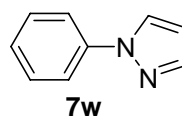
VJS-0606-9
Pulse Sequence: zgpg30



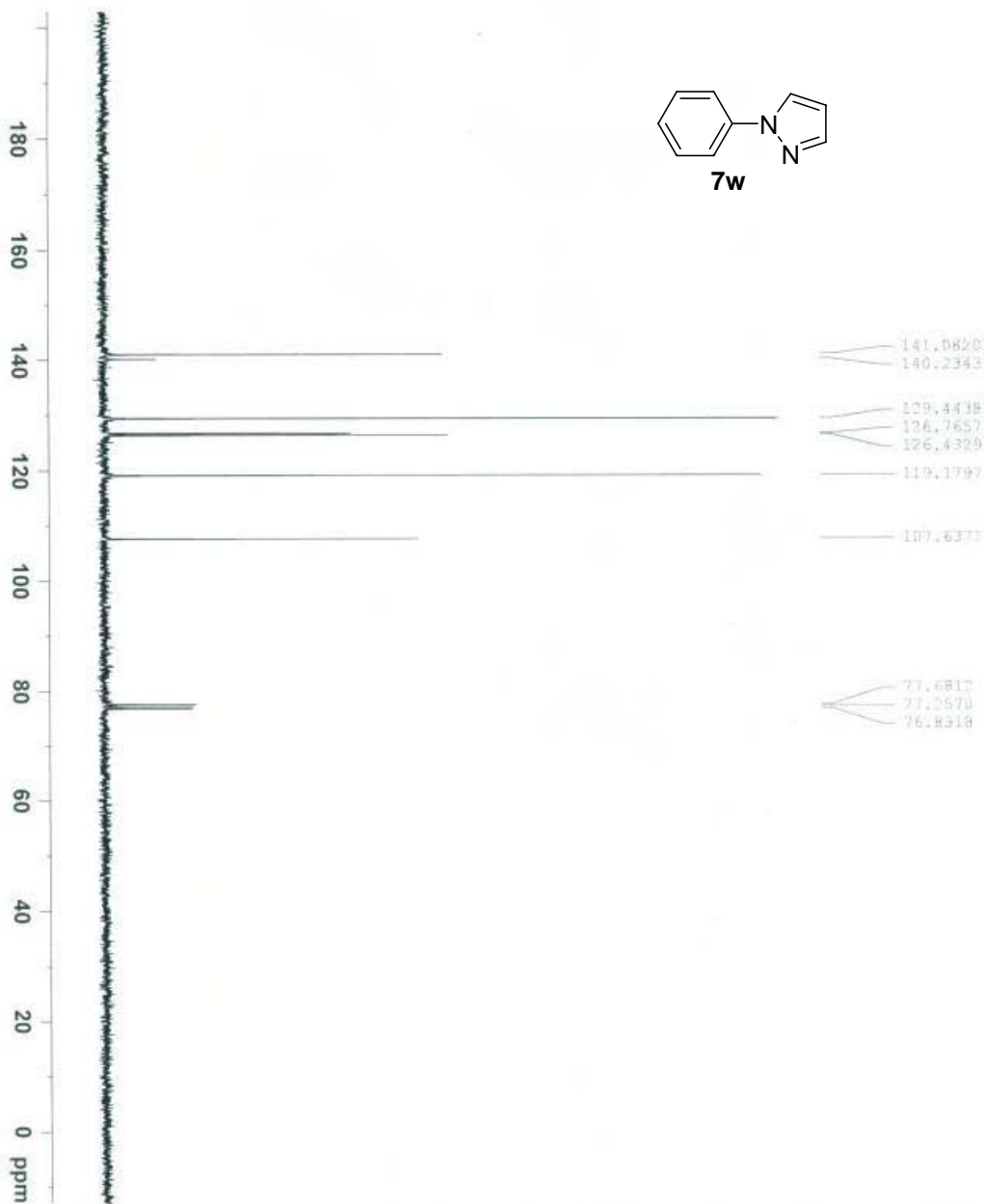
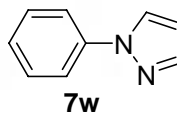
YJS-0606-9
Pulse Sequence: zgpg30



CV7 H1 CDCl3 2006-10-26
Pulse Sequence: zgpg30



CW7



Current Data Parameters
NAME CW7.13C
EXPNO 1
PROCNO 1

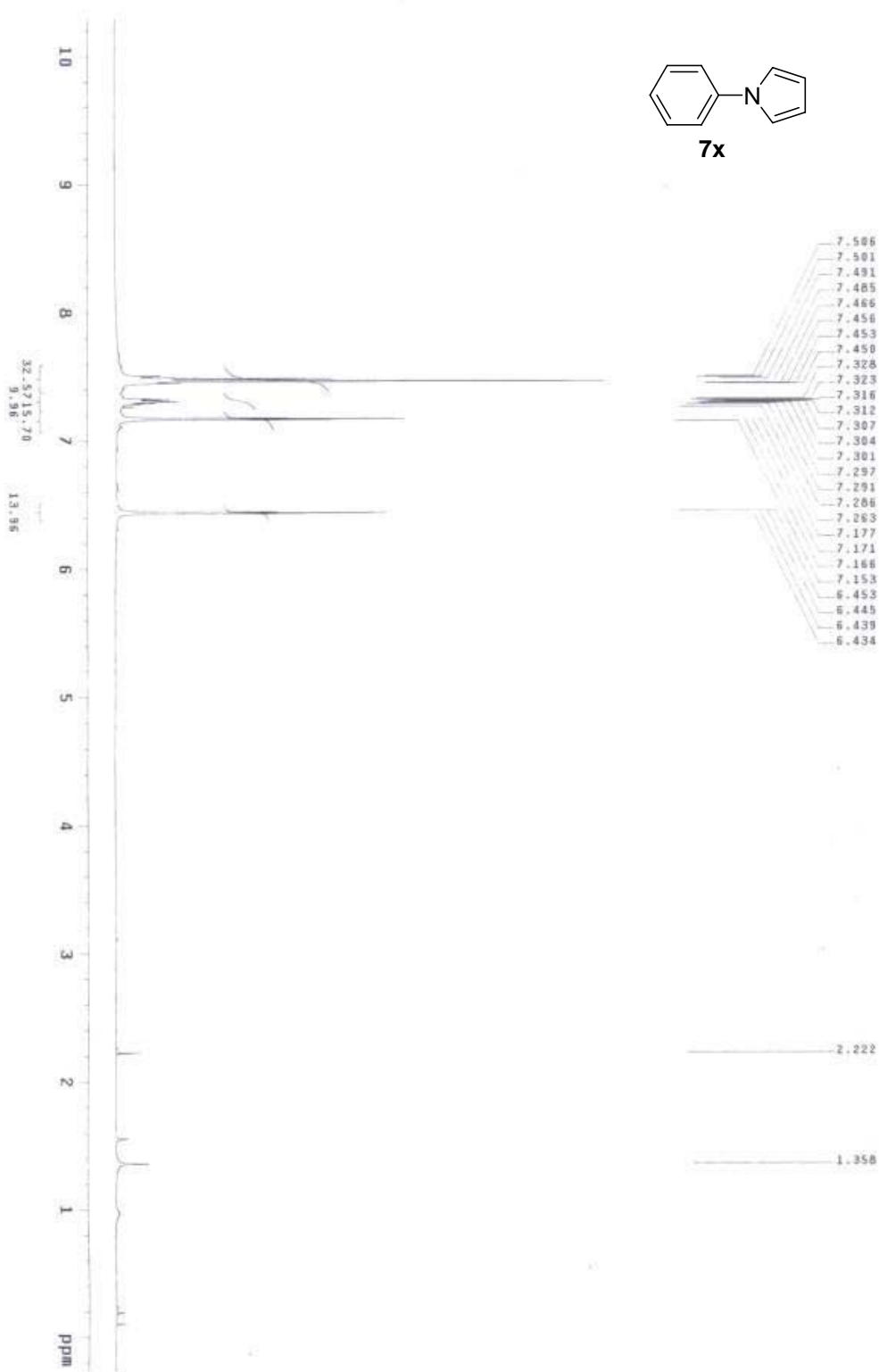
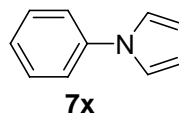
F2 - Acquisition Parameters
Date_ 20061036
Time_ 15:41
INSTRUM 5 mm PABBO BB-
PROBHD zgpg30
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 19
DS 16
SWH 16832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 5160.6
PC 26.550 usec
DE 6.00 usec
TE 297.5 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz

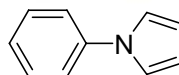
===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz

F2 - Processing parameters
SI 32768
SF 75.4677480 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

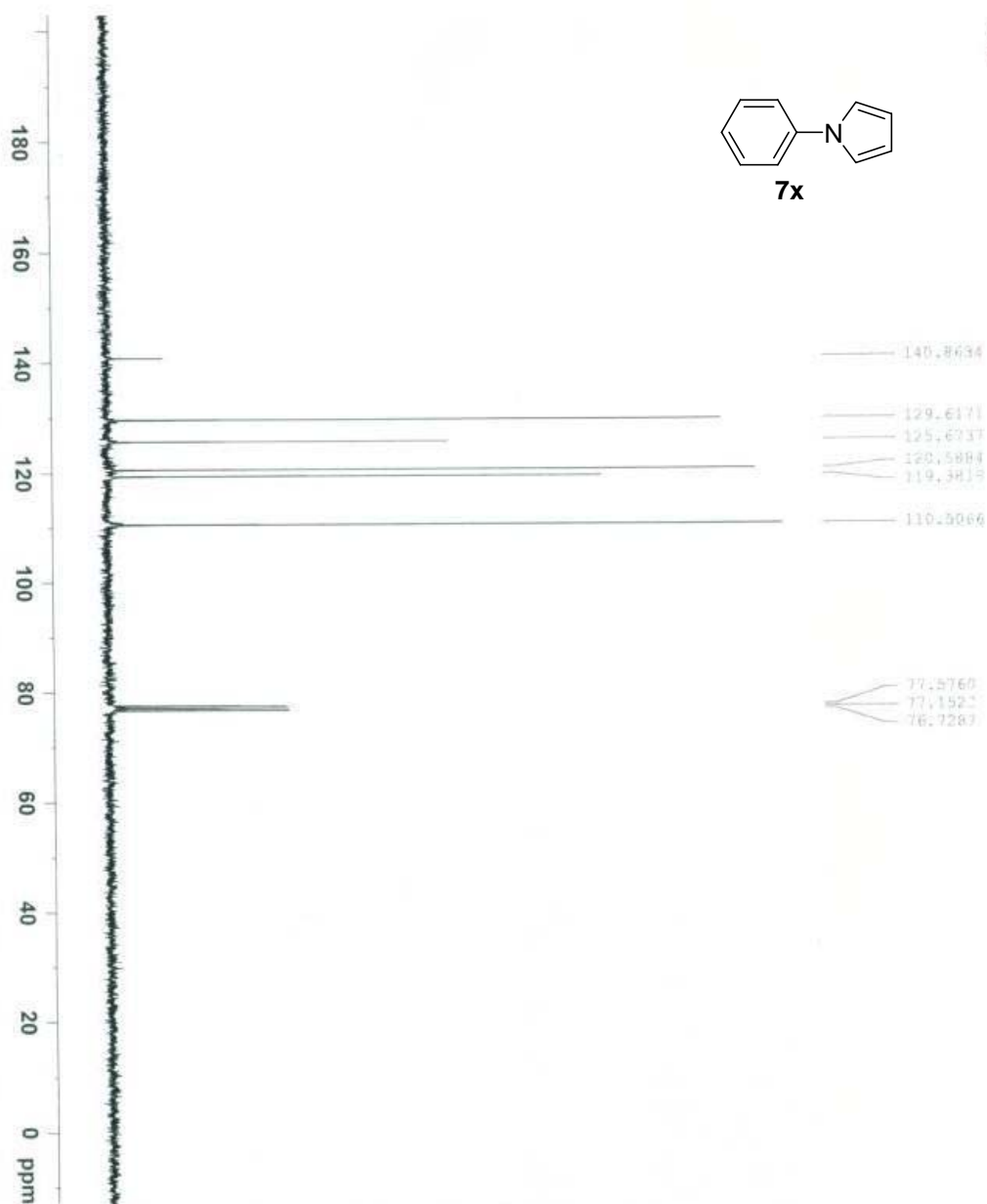
Exp# H1 CDCl3 2006-10-26
Pulse Sequence: zgpg1



CMB



7x



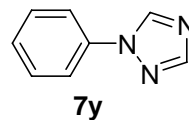
Current Data Parameters
 NAME CMB 13C
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20061026
 Time_ 15.34
 INSTRUM av300
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 FIDRES 0.0000000
 SOLVENT CDCl3
 NS 15
 DS 16
 SM 18832.388 Hz
 FIDRES 0.287360 Hz
 AQ 1.7400308 sec
 RG 5160.6
 DW 26.550 usec
 DE 6.00 usec
 TE 297.8 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 TD0 1

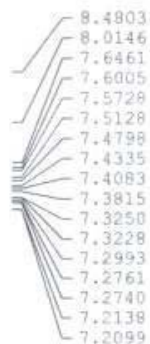
===== CHANNEL f1 =====
 NUC1 13C
 P1 6.00 usec
 PL1 -6.00 dB
 SFO1 75.475260 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 5.00 dB
 PL12 16.00 dB
 SFO2 300.1314410 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677490 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.40



Zlb29



Current Data Parameters
 NAME Zlb29
 EXPNO 1
 PROCNO 1

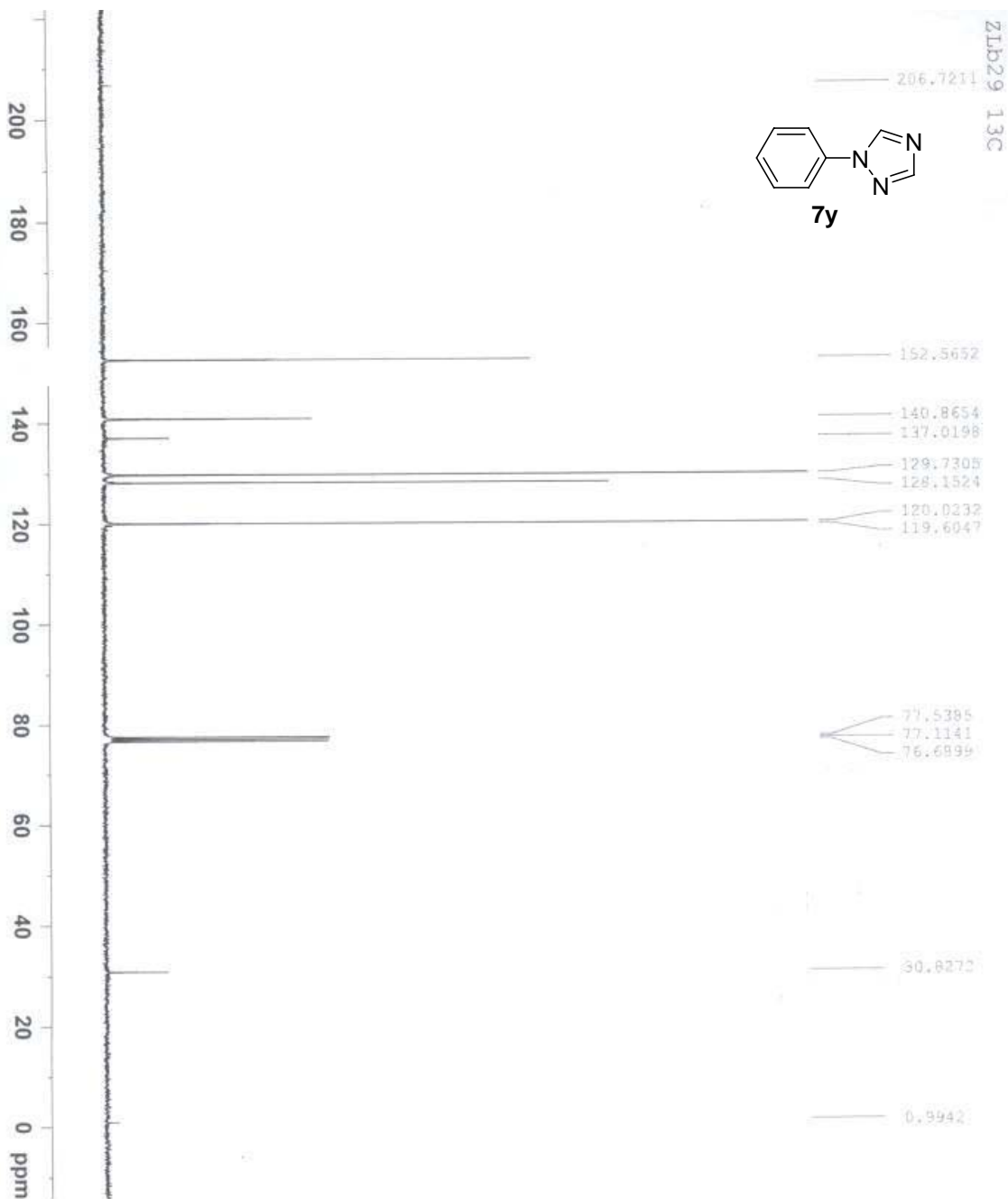
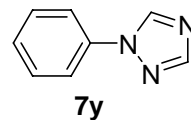
F2 - Acquisition Parameters

Date_ 20060803
 Time 11.18
 INSTRUM av300
 PROBD 5 mm PARBO BB-
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 4
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7328011 sec
 RG 101.6
 DW 83.400 usec
 DE 6.00 usec
 TE 297.9 K
 D1 2.50000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.70 usec
 PL1 -5.00 dB
 SFO1 300.1324010 MHz

F2 - Processing parameters
 SI 16384
 SF 300.1300236 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40





Current Data Parameters
NAME Zlb29 13C
EXPNO 1
PROCNO 1

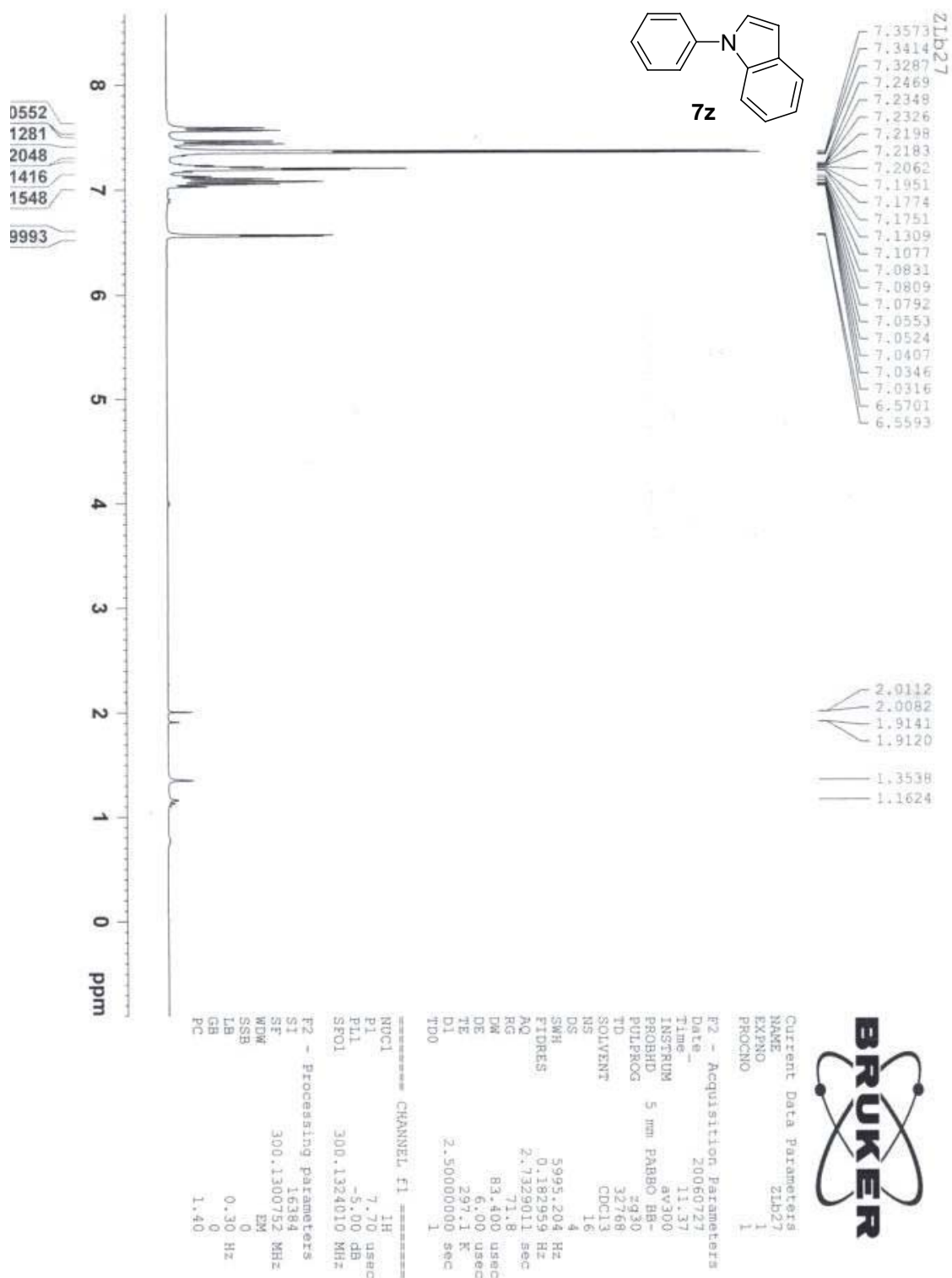
F2 - Acquisition Parameters
Date_ 20060803
Time 13.48

INSTRUM av300
PROBHD 5 mm PABBO HB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 960
DS 16
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 18390.4
DW 25.550 usec
DE 6.00 usec
TE 299.6 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1

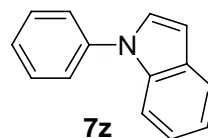
===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz

===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz

F2 - Processing Parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40



2lb27 13C



139.7625
136.0088
130.6507
129.7618
129.4401
125.0371
124.5245
124.4782
124.0180
122.4763
121.2538
120.4837
119.0152
110.6209
103.7090

77.5944
77.1711
76.7470

60.4749

30.9451

25.1103

14.3215



Current Data Parameters
NAME 2lb27 13C
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060731
Time 8.46
INSTRUM AV300
PROBHD 5 mm PABO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 590
DS 16
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 18390.4
RW 26.550 usec
DE 6.00 usec
TE 297.7 K
D1 1.00000000 sec
d11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 6.00 usec
PL1 -6.00 dB
SFO1 75.4752960 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -5.00 dB
PL12 16.00 dB
SFO2 300.1314410 MHz

F2 - Processing Parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40