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Acetylene-driven superbase-mediated self-organization of (het)arylpyridines from (het)aromatic nitriles

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General information.

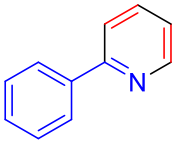
^{1}H (400 MHz), ^{13}C (101 MHz) and ^{15}N (41 MHz) NMR spectra were recorded on a Bruker AV400 instrument in $CDCl_3$. The ^{1}H and ^{13}C chemical shifts (δ) were referenced to $CDCl_3$ (7.27 ppm and 77.0 respectively). The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment and were referenced to CH_3NO_2 (0.0 ppm). Coupling constants (*J*) in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: s (singlet), d (doublet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets). Melting points (uncorrected) were measured on a SMP50 Stuart apparatus. Mass spectra of positive electron ionization ions (70 eV) were registered on a «LECO Pegasus BT» with a chromatograph «Agilent 8890».

Thin layer chromatography was carried out on Merck silica gel 60 F254 pre-coated aluminium foil sheets (eluent: diethyl ether/hexane = 1:3) and were visualized using UV light (254 nm).

Synthesis of pyridines 2 (general procedure).

A mixture of nitrile **1** (5 mmol), $KOH{\cdot}0.5H_2O$ (5 mmol, 0.32 g), and MeOH (5 mmol, 0.16 g) in DMSO with 0.05% of water content (50 mL) was placed into a 0.25 dm^3 steel Parr reactor equipped with mechanical stirrer, manometer, and gas inlet valve for charging acetylene. The reactor was fed with acetylene under pressure ~ 3 atm from commercially available acetylene cylinder and then decompressed to atmospheric pressure to remove air. The reactor was fed with acetylene again (~ 14 atm), the reaction mixture was stirred at room temperature for 5 min (acetylene pressure dropped up to ~3-4 atm) and heated (heating mantle) at 90 ºC for 10 min. After cooling to room temperature, the mixture was diluted with water (100 mL) and extracted with diethyl ether (4 × 45 mL). Diethyl ether extracts were washed with H_2O (3 × 15 mL) and evaporated under reduced pressure. The pure pyridines **2a-k** were obtained by column chromatography (basic Al_2O_3, eluent: *n*-hexane/diethyl ether with gradient from 1:0 to 1:1).

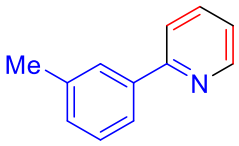
2-Phenylpyridine 2a[S1]



Following the general procedure, **2a** was prepared from **1a** (5 mmol, 0.52 g). **2a** was isolated as pale-yellow oil (0.280 g, 36% yield). ^{1}H NMR ($CDCl_3$) δ: 8.73-8.70 (m, 1H, H6), 8.02-8.00 (m, 2H, H^o), 7.76-7.74 (m, 2H, H3, H4), 7.51-7.48 (m, 2H, H^m), 7.44-7.41 (m, 1H, H^p), 7.25-7.22 (m, 1H, H5).

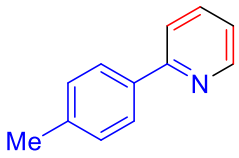
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 157.5 (C2), 149.7 (C6), 139.4 (C^i), 136.7 (C4), 128.9 (C^p), 128.7 (C^m), 126.9 (C^o), 122.0 (C3), 120.5 (C5). ^{15}N NMR, δ: -74.5. MS (EI): m/z calcd for $C_{11}H_9N$ 155.073 $[M]^{+\cdot}$; found 155.084 (100.0 %).

2-(*m*-Tolyl)pyridine 2b[S2]



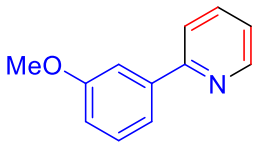
Following the general procedure, **2b** was prepared from **1b** (5 mmol, 0.586 g). **2b** was isolated as pale-yellow oil (0.262 g, 31% yield). ^{1}H NMR ($CDCl_3$) δ: 8.71-8.70 (m, 1H, H6), 7.86 (s, 1H, H^2), 7.78-7.72 (m, 3H, H3, H4, H^4), 7.40-7.36 (m, 1H, H^5), 7.26-7.21 (m, 2H, H5, H^6), 2.45 (s, 3H, 3-Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 157.7 (C2), 149.6 (C6), 139.4 (C^1), 138.4 (C3), 136.7 (C4), 129.7 (C^4), 128.6 (C^5), 127.6 (C^2), 124.0 (C^6), 122.0 (C3), 120.6 (C5), 21.5 (3-Me). MS (EI): m/z calcd for $C_{12}H_{11}N$ 169.089 $[M]^{+\cdot}$; found 169.017 (100.0 %).

2-(*p*-Tolyl)pyridine 2c[S3]



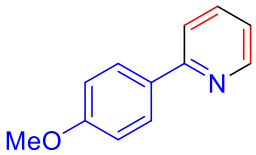
Following the general procedure, **2c** was prepared from **1c** (5 mmol, 0.586 g). **2c** was isolated as pale-yellow oil (0.254 g, 30% yield). ^{1}H NMR ($CDCl_3$) δ: 8.70-8.69 (m, 1H, H6), 7.93-7.91 (m, 2H, H^o), 7.74-7.69 (m, 2H, H3, H4), 7.31-7.29 (m, 2H, H^m), 7.21-7.18 (m, 1H, H5), 2.42 (s, 3H, 4-Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 157.4 (C2), 149.5 (C6), 138.8 (C^p), 136.6 (C^i, C4), 129.4 (C^m), 126.7 (C^o), 121.7 (C5), 120.1 (C3), 21.2 (4-Me). MS (EI): m/z calcd for $C_{12}H_{11}N$ 169.089 $[M]^{+\cdot}$; found 169.032 (100.0 %).

2-(3-Methoxyphenyl)pyridine 2d[S4]



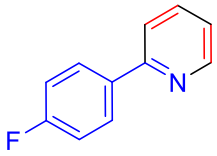
Following the general procedure, **2d** was prepared from **1d** (5 mmol, 0.66 g). **2d** was isolated as pale-yellow oil (0.259 g, 28% yield). ^{1}H NMR ($CDCl_3$) δ:8.71-8.70 (m, 1H, H6), 7.78-7.72 9 (m, 2H, H3, H4), 7.60 (br. s, 1H, H^2), 7.57-7.54 (m, 1H, H^6), 7.42-7.37 (m, 1H, H^5), 7.26-7.23 (m, 1H, H5), 7.00-6.97 (m, 1H, H^4), 3.91 (s, 3H, OMe). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ: 160.1 (C^3), 157.2 (C2), 149.6 (C6), 140.9 (C^1), 136.7 (C4), 129.7 (C^5), 122.2 (C5), 120.6 (C3), 119.3 (C^6), 115.0 (C^4), 112.0 (C^2), 55.3 (OMe). ^{15}N NMR, δ: -74.0. MS (EI): m/z calcd for $C_{12}H_{11}NO$ 185.084 $[M]^{+\cdot}$; found 185.020 (73.43 %).

2-(4-Methoxyphenyl)pyridine 2e[S5]



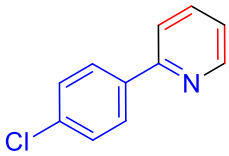
Following the general procedure, **2e** was prepared from **1e** (5 mmol, 0.66 g). **2e** was isolated as white powder (0.268 g, 29% yield). M.p. 53.0-55.0 ^{o}C. ^{1}H NMR ($CDCl_3$) δ: 8.67-8.66 (m, 1H, H6), 7.98-7.95 (m, 2H, H^{o}), 7.74-7.66 (m, 2H, H3, H4), 7.20-7.16 (m, 1H, H5), 7.02-7.00 (m, 2H, H^{m}), 3.88 (s, 3H, OMe). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 160.4 (C^{p}), 157.1 (C2), 149.5 (C6), 136.6 (C4), 132.0 (C^{i}), 128.1 (C^{m}), 121.4 (C5), 119.8 (C3), 114.1 (C^{o}), 55.3 (4-OMe). MS (EI): m/z calcd for $C_{12}H_{11}NO$ 185.084 $[M]^{+\cdot}$; found 185.092 (100.0 %).

2-(4-Fluorophenyl)pyridine 2f[S2]



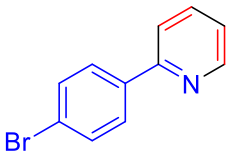
Following the general procedure (using 5 mmol of Bu^{t}OH instead of MeOH), **2f** was prepared from **1f** (5 mmol, 0.61 g). **2f** was isolated as pale-yellow oil (0.130 g, 15% yield). ^{1}H NMR ($CDCl_3$) δ: 8.70-8.68 (m, 1H, H6), 8.01-7.98 (m, 2H, H^{o}), 7.78-7.74 (m, 1H, H4), 7.70-7.68 (m, 1H, H3), 7.25-7.22 (m, 1H, H5), 7.19-7.15 (m, 2H, H^{m}). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 163.5 (d, *J* = 248.2 Hz, C^{p}), 156.4 (C2), 149.6 (C6), 136.8 (C4), 135.5 (d, *J* = 2.8 Hz, C^{i}), 128.7 (d, *J* = 8.3 Hz, C^{o}), 122.0 (C5), 120.3 (C3), 115.6 (d, *J* = 21.6 Hz, C^{m}). MS (EI): m/z calcd for $C_{11}H_8FN$ 173.064 $[M]^{+\cdot}$; found 173.074 (100.0 %).

2-(4-Chlorophenyl)pyridine 2g[S5]



Following the general procedure, **2g** was prepared from **1g** (5 mmol, 0.69 g). **2g** as pale-yellow oil (0.171 g, 18% yield) and **2e** (0.120 g, 13% yield) were isolated. **2g**: ^{1}H NMR ($CDCl_3$) δ: 8.71-8.69 (m, 1H, H6), 7.95 (d, *J* = 8.6 Hz, 2H, H^{o}), 7.79-7.75 (m, 1H, H4), 7.72-7.70 (m, 1H, H3), 7.46 (d, *J* = 8.6 Hz, 2H, H^{m}), 7.26-7.24 (m, 1H, H5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 156.2 (C2), 149.7 (C6), 137.8 (C^{i}), 136.8 (C4), 135.1 (C^{p}), 128.9 (C^{m}), 128.1 (C^{o}), 122.3 (C5), 120.3 (C3). MS (EI): m/z calcd for $C_{11}H_8ClN$ 189.035 $[M]^{+\cdot}$; found 189.054 (100.0 %).

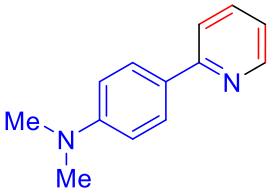
2-(4-Bromophenyl)pyridine 2h[S5]



Following the general procedure, **2h** was prepared from **1h** (2.5 mmol, 0.45 g). **2h** as colorless crystals (0.222 g, 19% yield) and **2e** (0.09 g, 10% yield) were isolated. **2h**: ^{1}H NMR ($CDCl_3$) δ: 8.71-8.69 (m, 1H, H6), 7.90-7.87 (m, 2H, H^{o}), 7.79-7.74 (m, 1H, H4), 7.72-7.70 (m, 1H, H3), 7.63-7.60 (m, 1H, H^{m}), 7.26-7.24 (m, 1H, H5). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 156.3 (C2), 149.8 (C6), 138.3 (C^{i}),

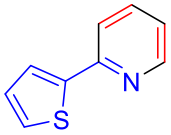
136.9 (C4), 131.9 (C^m), 128.4 (C^o), 123.4 (C^p), 122.4 (C5), 120.3 (C3). MS (EI): m/z calcd for $C_{11}H_8BrN$ 232.984 $[M]^{+\cdot}$; found 233.067 (89.39 %).

_N,N_-Dimethyl-4-(pyridin-2-yl)aniline 2i[S6]



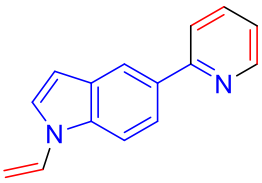
Following the general procedure, **2i** was prepared from **1i** (5 mmol, 0.73 g). **2i** was isolated as pale-yellow powder (0.180 g, 18% yield). M.p. 75.0-82.0 °C. ^{1}H NMR ($CDCl_3$) δ: 8.64-8.62 (m, 1H, H6), 7.93 (d, *J* = 8.9 Hz, 2H, H^o), 7.68-7.65 (m, 2H, H3, H4), 7.12-7.09 (m, 1H, H5), 6.81 (d, *J* = 8.9 Hz, 1H, H^m), 3.03 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 157.5 (C2), 151.0 (C^p), 149.3 (C6), 136.4 (C4), 127.7 (C^m), 127.2 (C^i), 120.5 (C5), 119.1 (C3), 112.2 (C^o), 40.3 (NMe_2). MS (EI): m/z calcd for $C_{13}H_{14}N_2$ 198.116 $[M]^{+\cdot}$; found 198.102 (100.0 %).

2-(Thiophen-2-yl)pyridine 2j[S7]



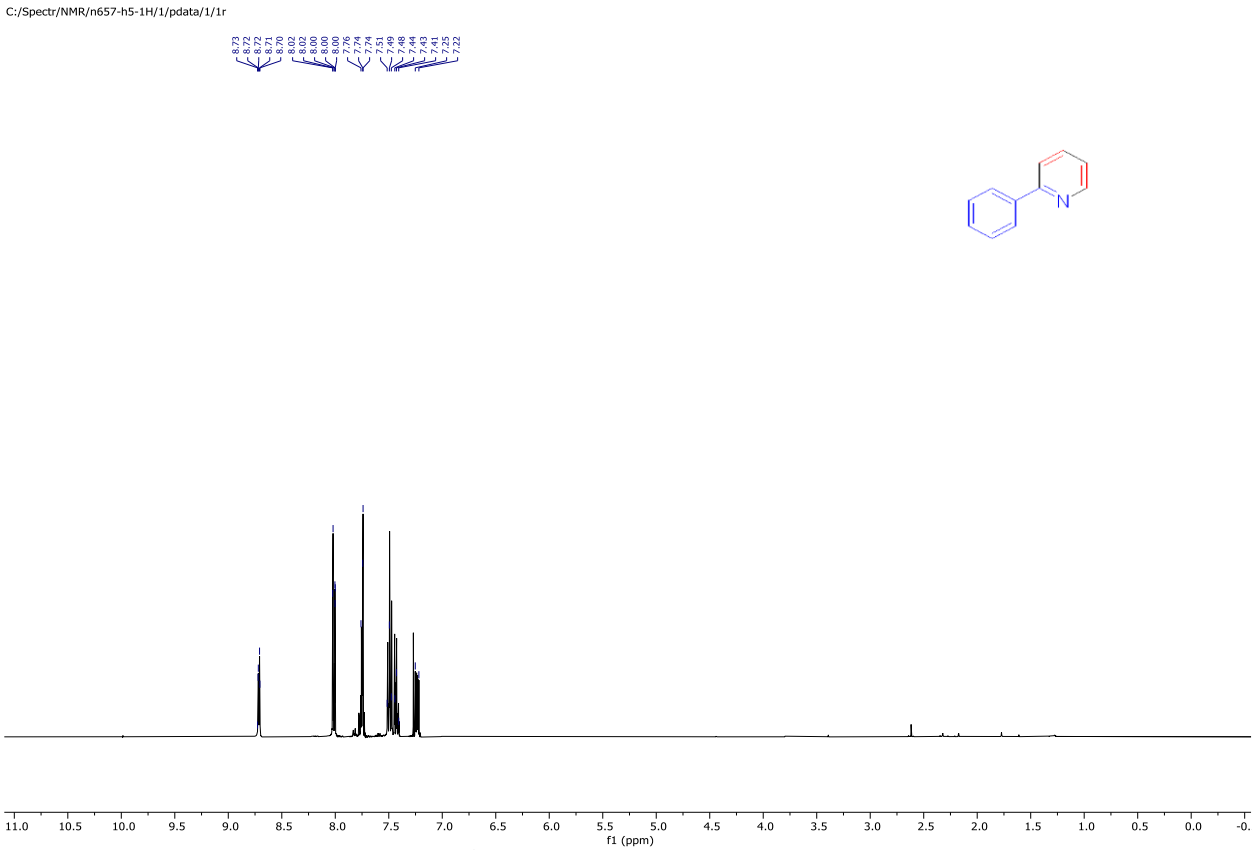
Following the general procedure, **2j** was prepared from **1j** (5 mmol, 0.54 g). **2j** was isolated as pale-yellow oil (0.105 g, 13% yield). ^{1}H NMR ($CDCl_3$) δ: 8.58-8.56 (m, 1H, H6), 7.69-7.64 (m, 2H, H3, H4), 7.58 (dd, *J* = 3.7, 1.1 Hz, 1H, H^3), 7.40 (dd, *J* = 5.1, 1.1 Hz, 1H, H^5), 7.15-7.10 (m, 2H, H5, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 152.5 (C2), 149.5 (C6), 144.8 (C^2), 136.6 (C4), 128.0 (C^4), 127.5 (C^5), 124.4 (C^3), 121.8 (C5), 118.7 (C3). ^{15}N NMR, δ: -79.2. MS (EI): m/z calcd for C_9H_7NS 161.030 $[M]^{+\cdot}$; found 161.055 (100.0 %).

5-(Pyridin-2-yl)-1-vinyl-1*H*-indole 2k

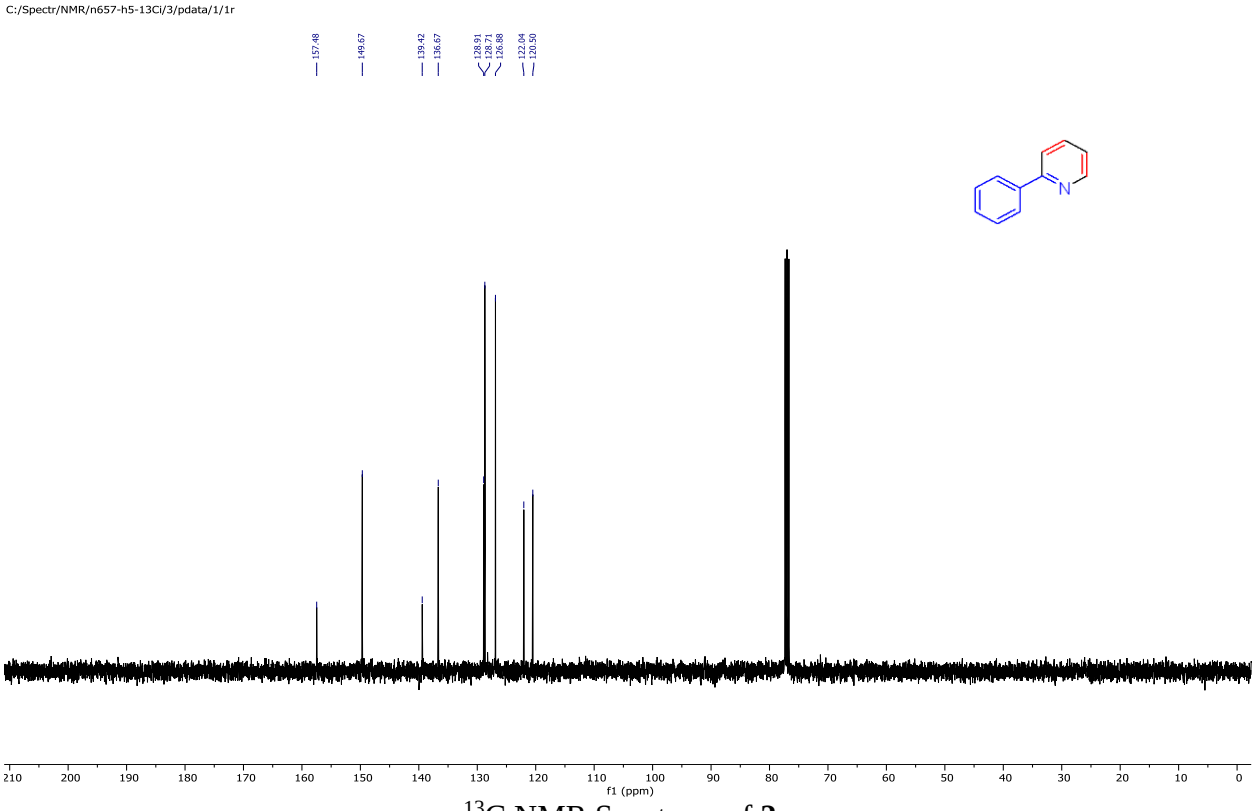


Following the general procedure, **2k** was prepared from 5-cyano-1*H*-indole **1k** (3 mmol, 0.41 g). **2k** was isolated as pale-yellow powder (0.154 g, 14% yield). M.p. 81.0-55.0 °C. ^{1}H NMR ($CDCl_3$) δ: 8.71-8.69 (m, 1H, H6), 8.27-8.26 (m, 1H, H^4), 7.96 (dd, *J* = 8.7, 1.8 Hz, 1H, H^6), 7.81-7.73 (m, 2H, H3, H4), 7.56 (d, *J* = 8.7 Hz, 1H, H^7), 7.47 (d, *J* = 3.4 Hz, 1H, H^2), 7.27 (dd, *J* = 15.7, 9.0 Hz, 1H, C<u>H</u>=CH_2), 7.22-7.18 (m, 1H, H5), 6.72 (d, *J* = 3.4 Hz, 1H, H^3), 5.24 (dd, *J* = 15.7, 1.4 Hz, 1H, CH=C<u>H</u>$_2$), 4.82 (dd, *J* = 9.0, 1.4 Hz, 1H, CH=C<u>H</u>$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 158.3 (C2), 149.5 (C6), 136.6 (C4), 136.0 (C^{7a}), 132.4 (C^5), 129.6 (C^{4a}), 129.5 (=CH), 124.1, 122.0, 121.3, 120.3, 119.9 (C^2, C3, C^6, C5, C^4) 109.7 (C^7), 105.6 (C^3), 96.9 (=CH_2). MS (EI): m/z calcd for $C_{15}H_{12}N_2$ 220.100 $[M]^{+\cdot}$; found 220.133 (100.0 %).

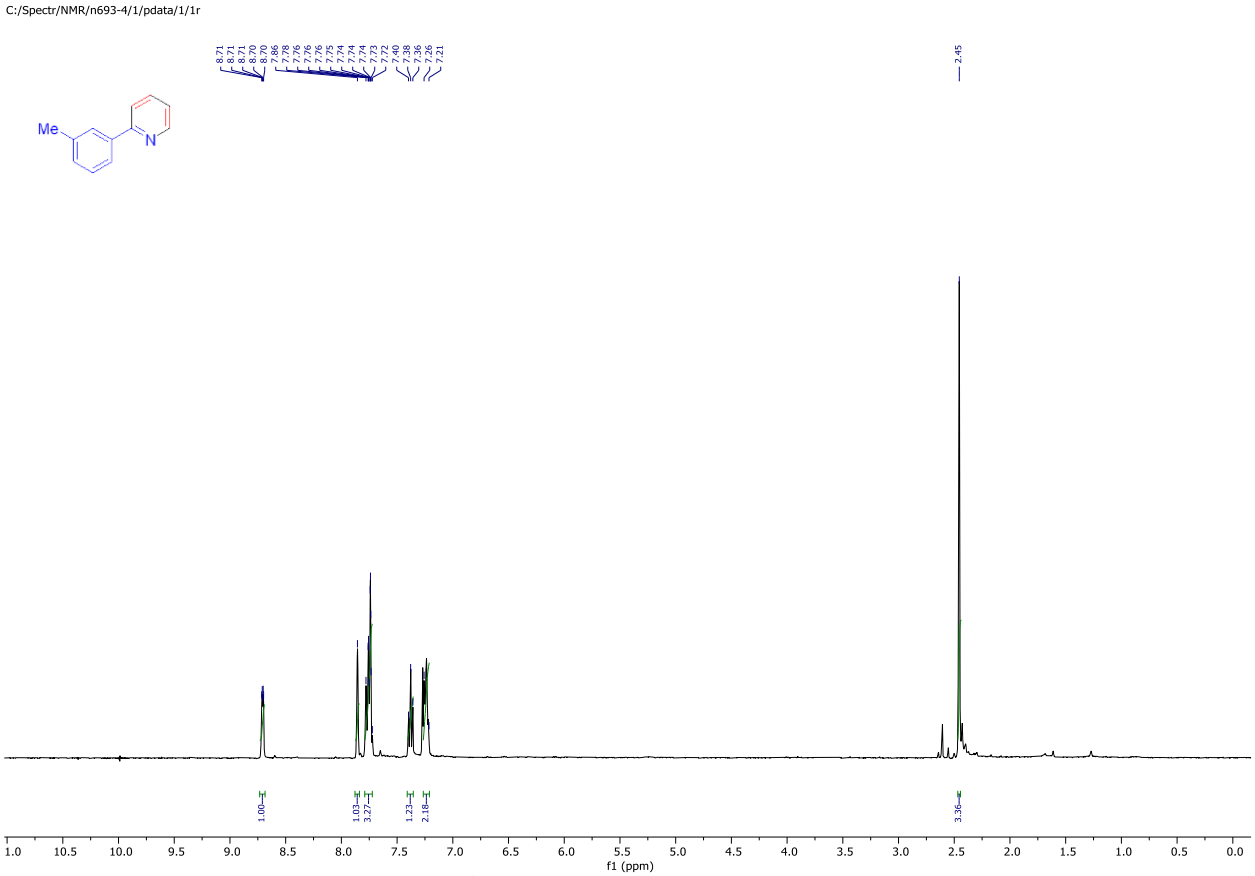
NMR Spectra



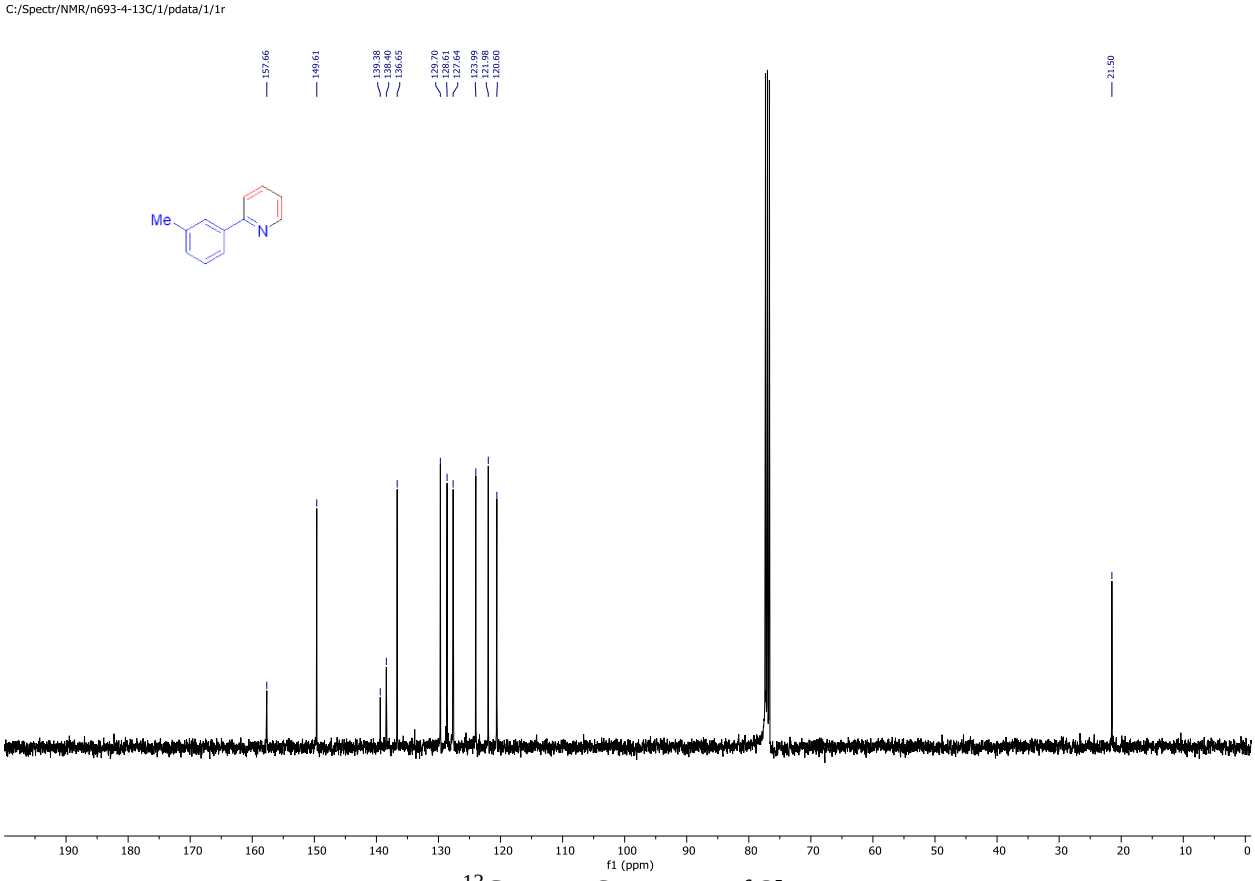
^{1}H NMR Spectrum of **2a**



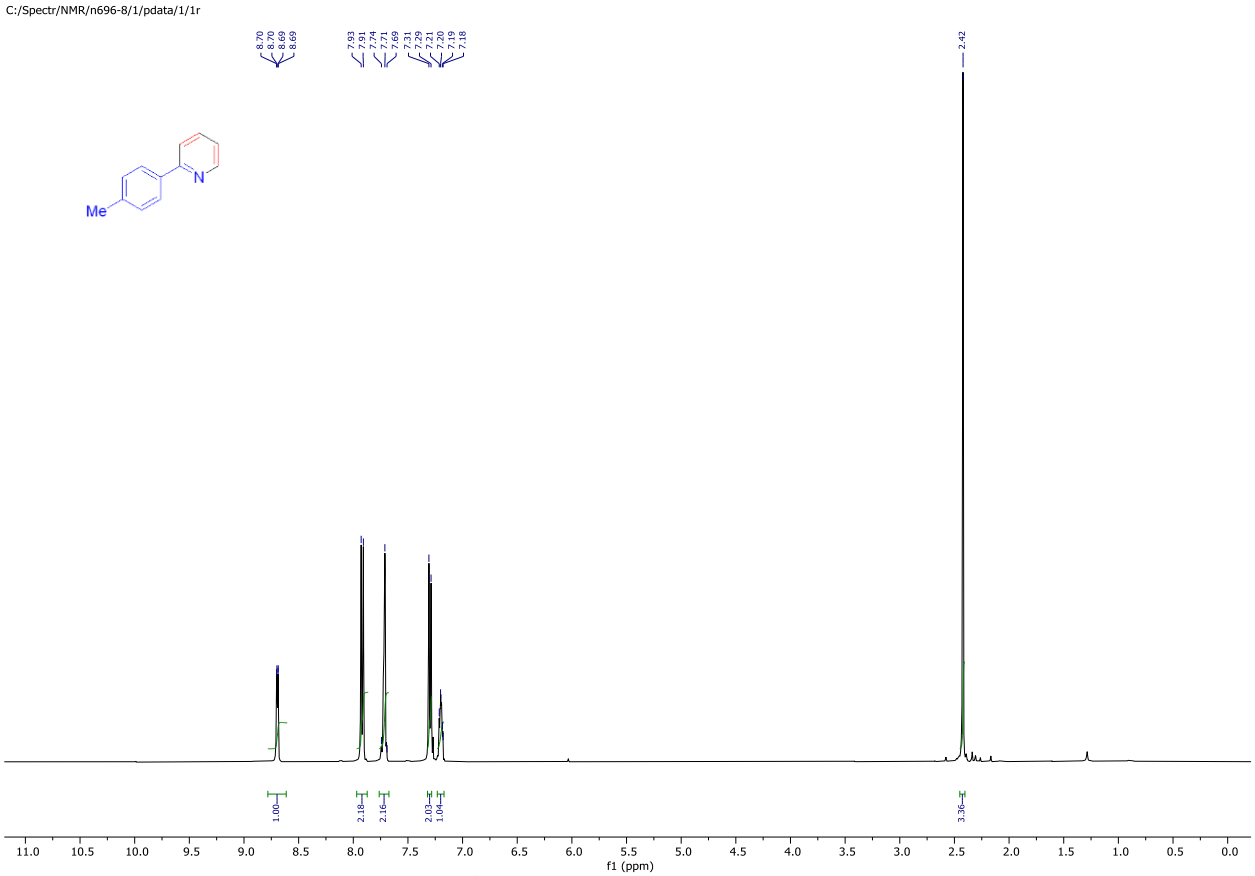
^{13}C NMR Spectrum of **2a**



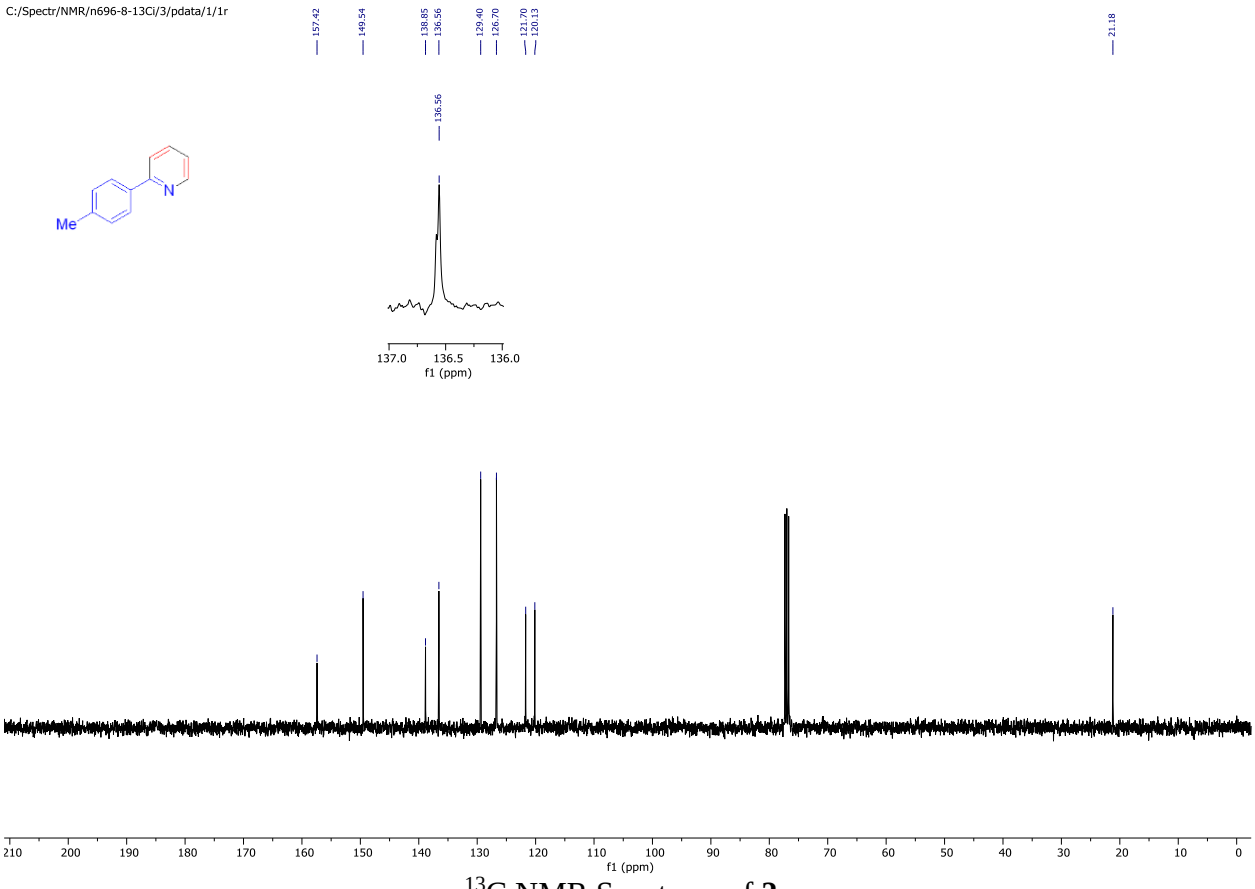
^{1}H NMR Spectrum of **2b**



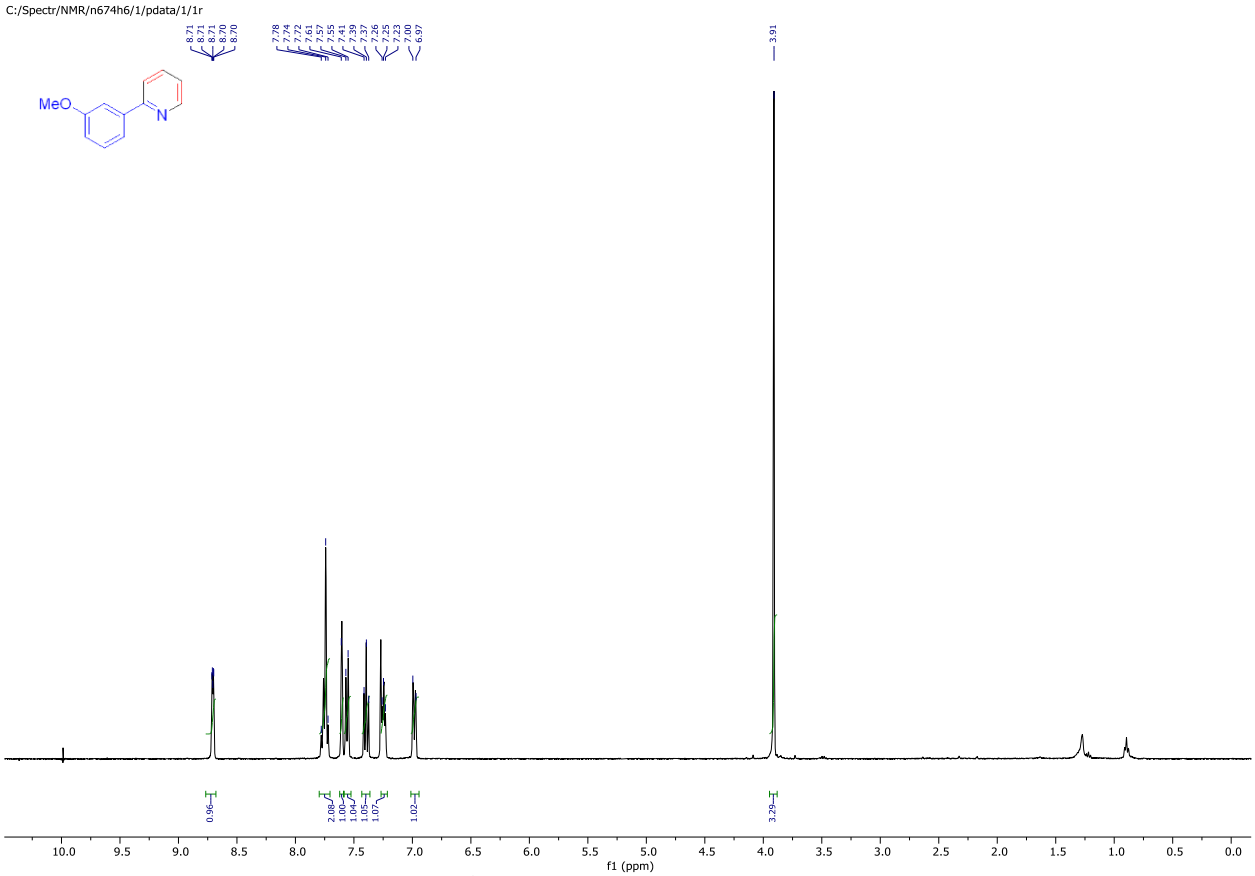
^{13}C NMR Spectrum of **2b**



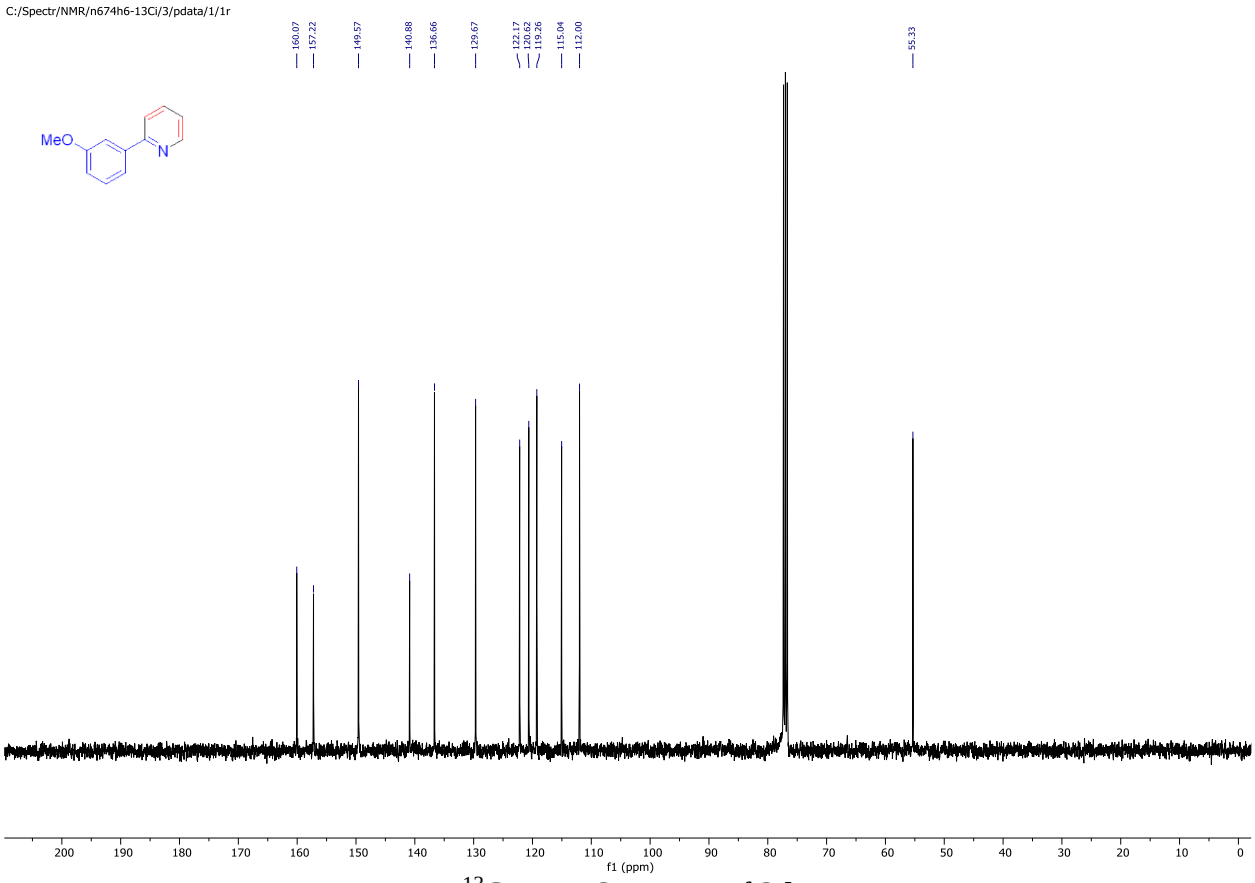
^{1}H NMR Spectrum of **2c**



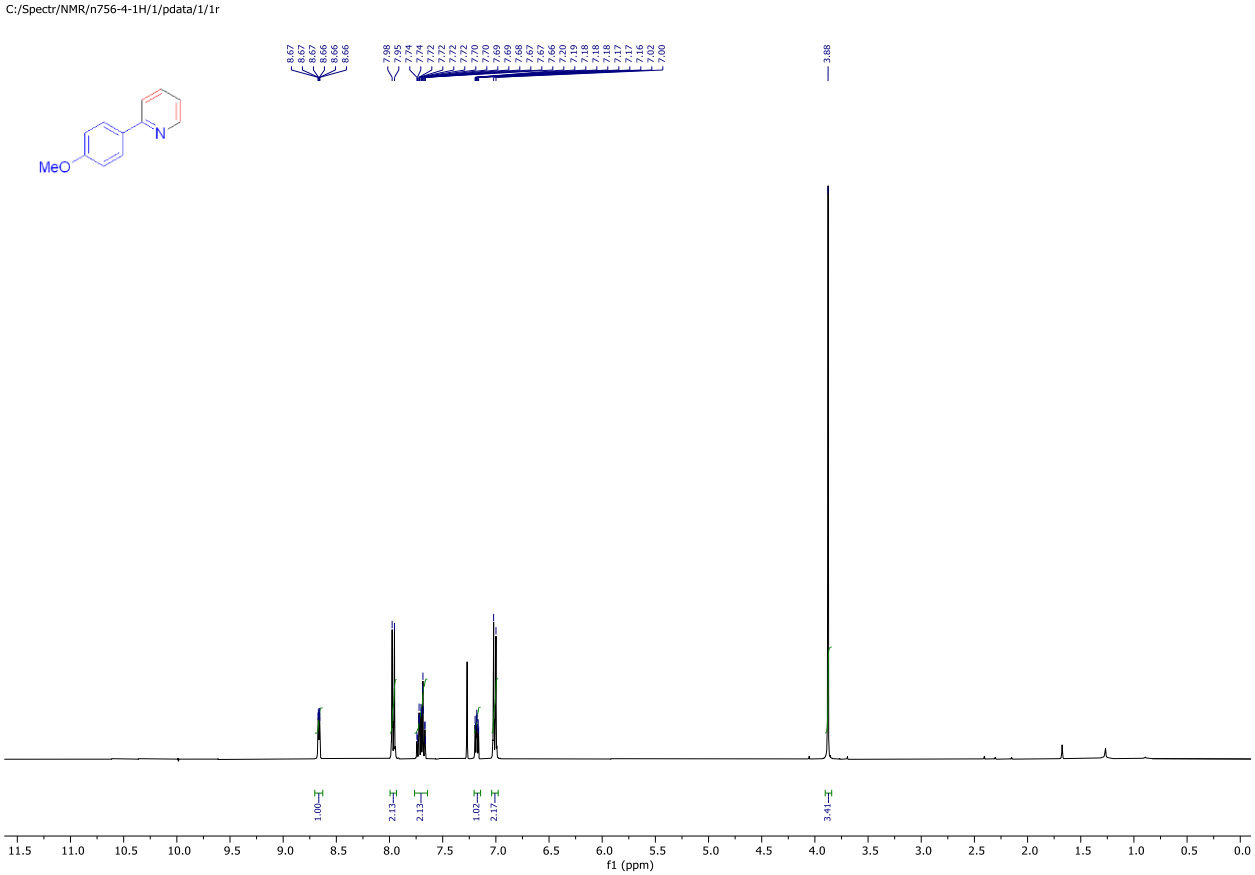
^{13}C NMR Spectrum of **2c**



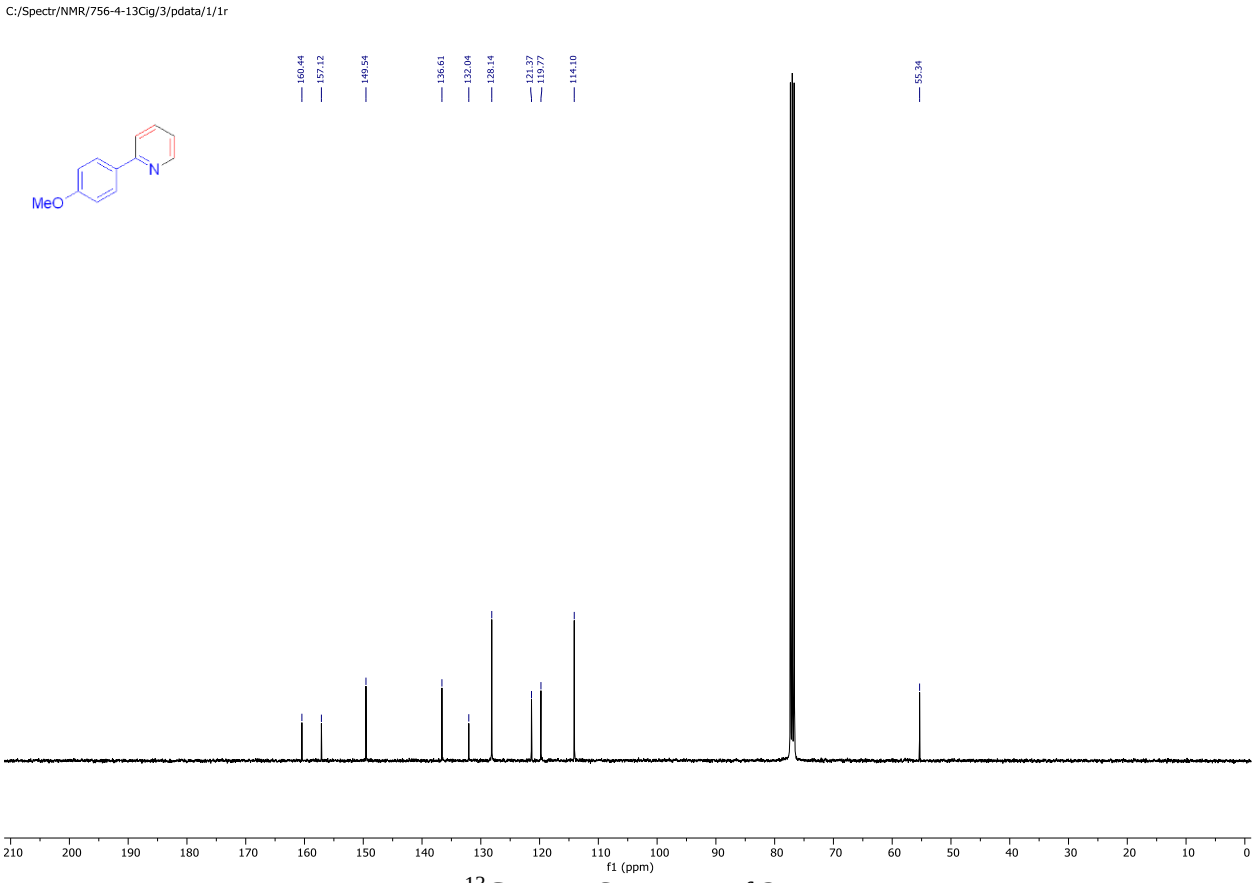
^{1}H NMR Spectrum of **2d**



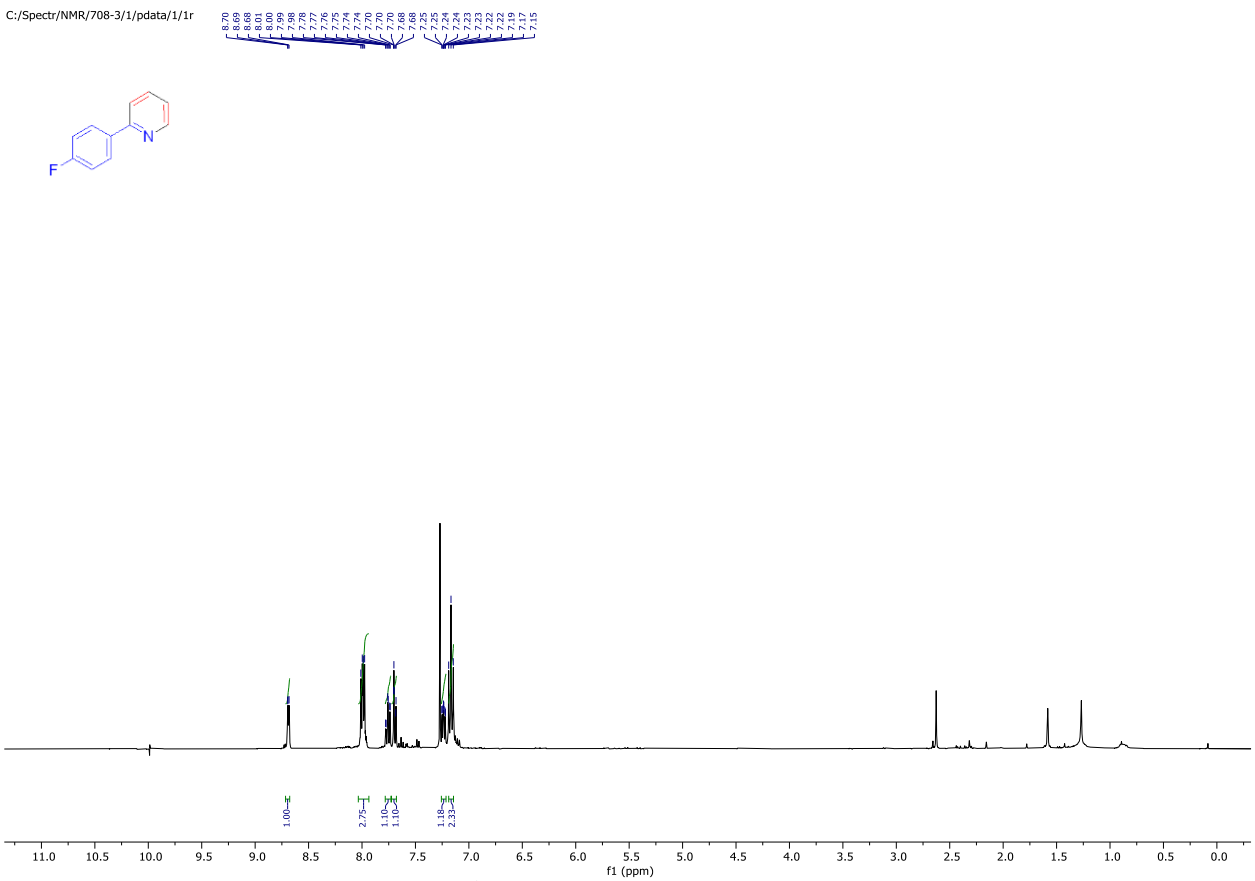
^{13}C NMR Spectrum of **2d**



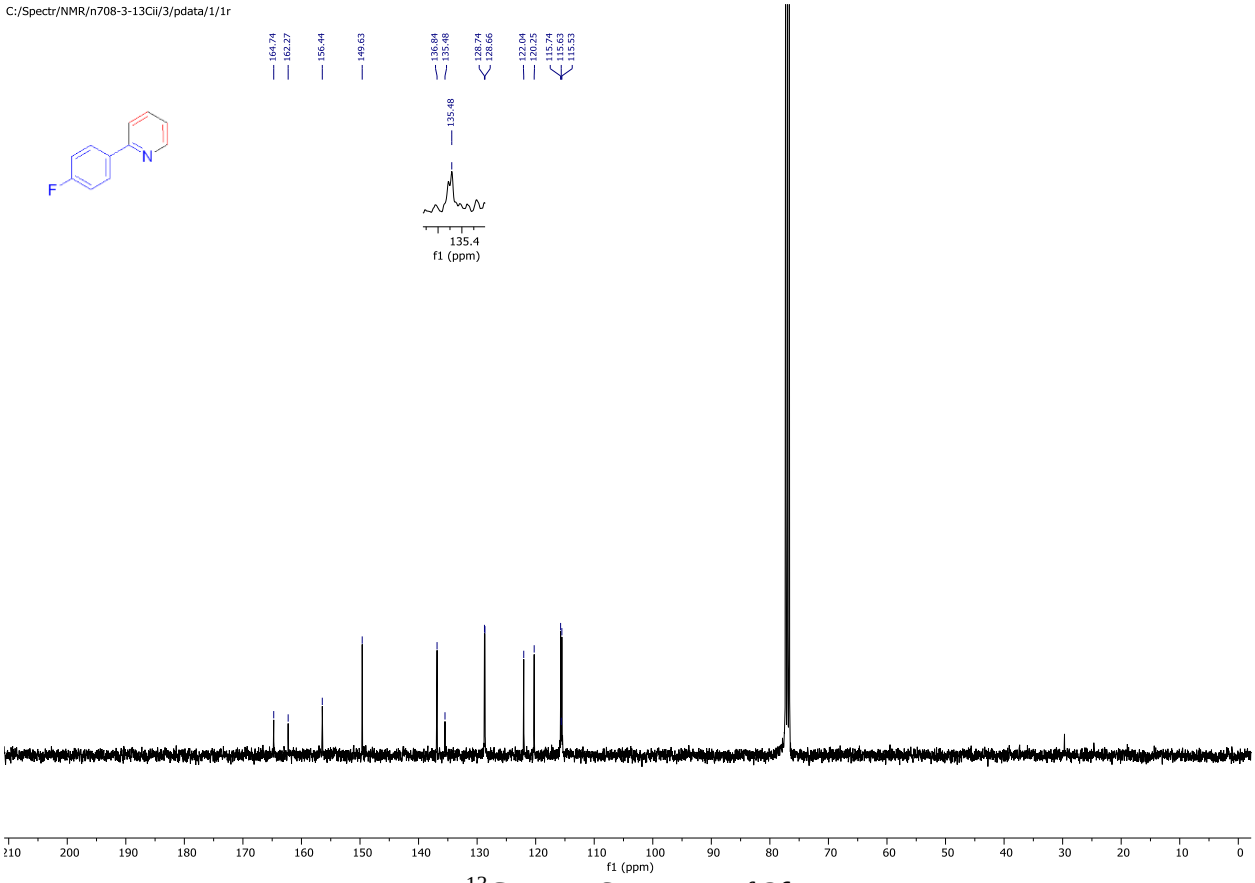
^{1}H NMR Spectrum of **2e**



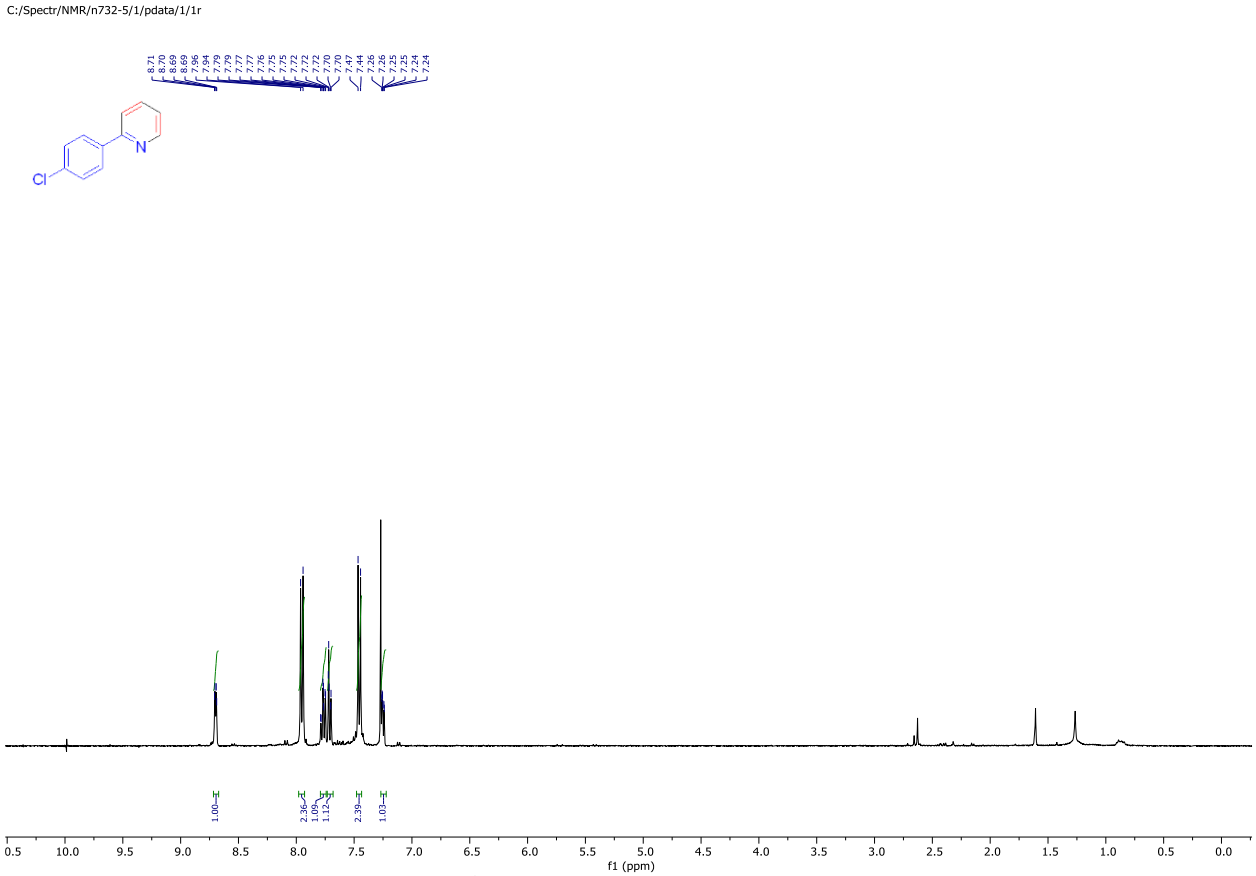
^{13}C NMR Spectrum of **2e**



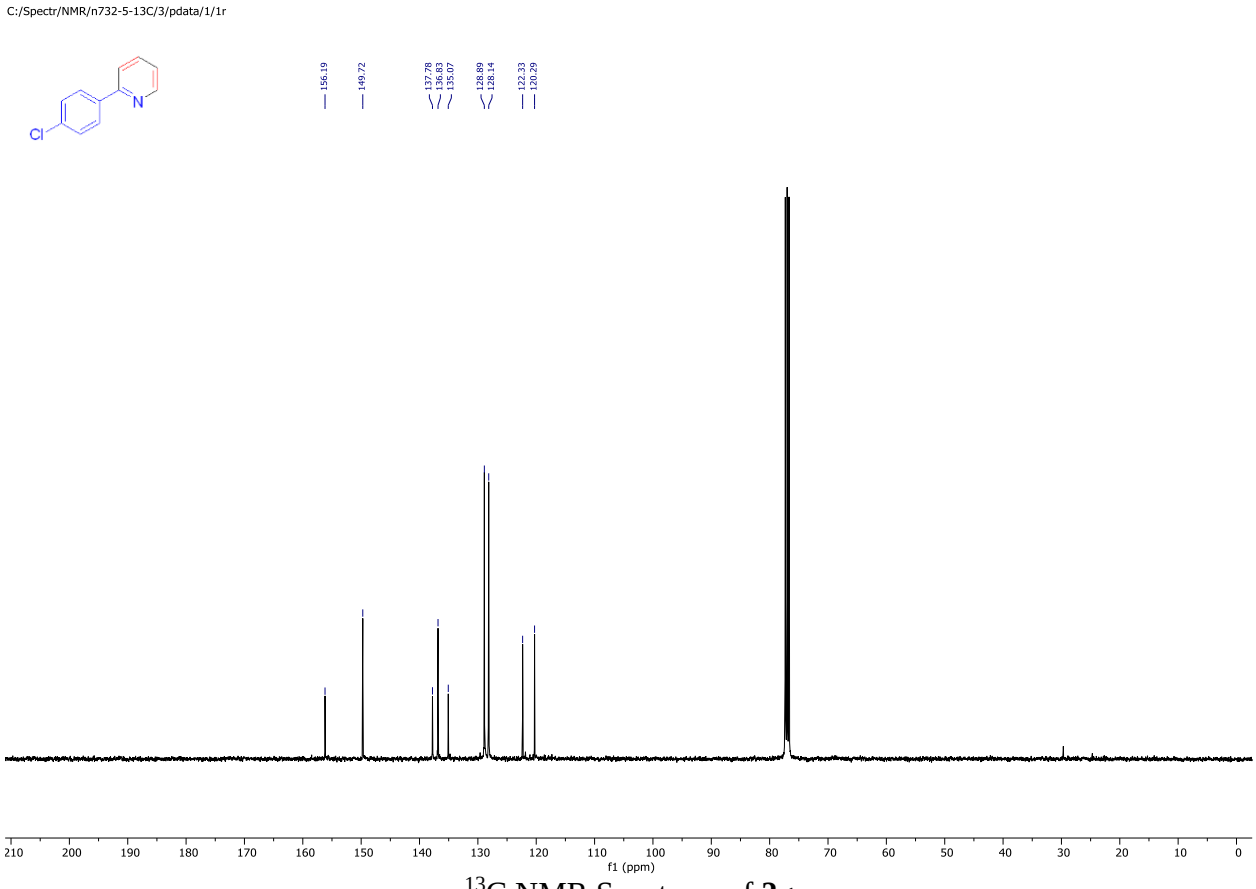
^{1}H NMR Spectrum of **2f**



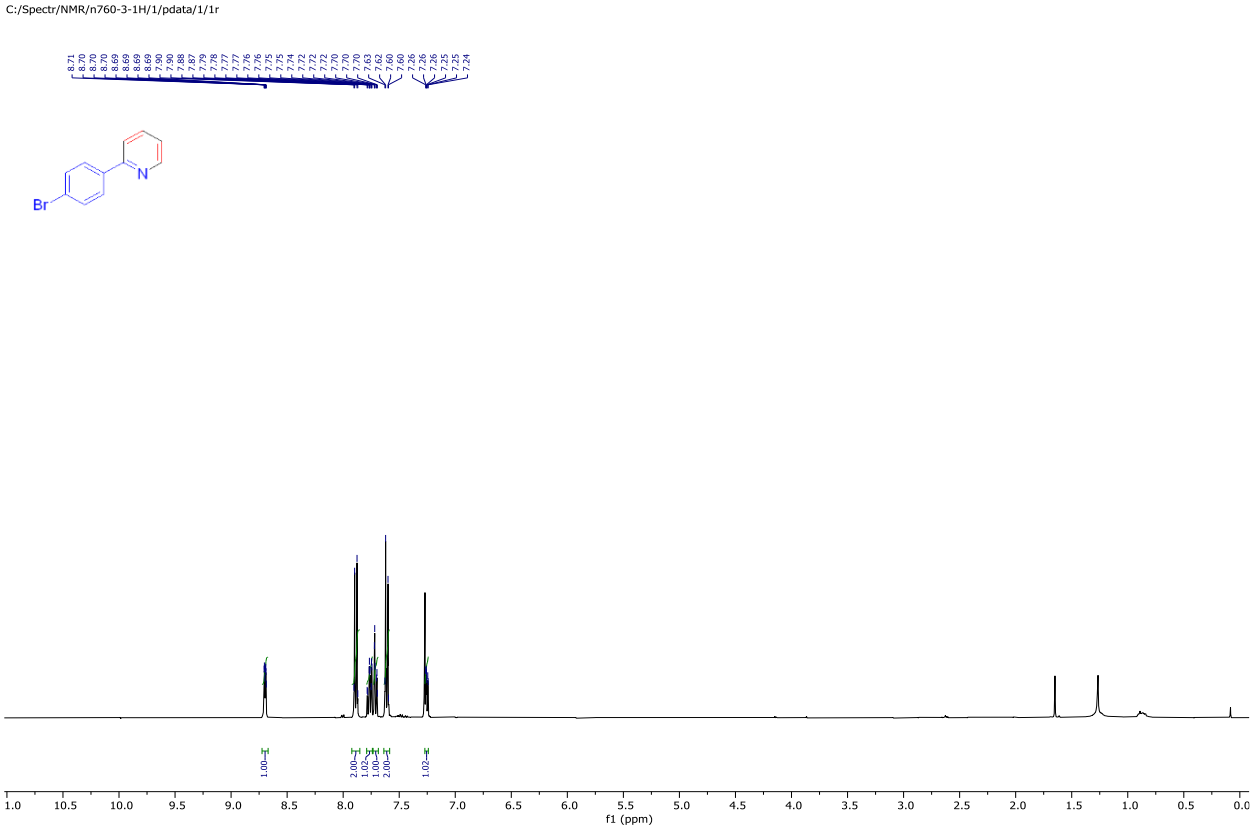
^{13}C NMR Spectrum of **2f**



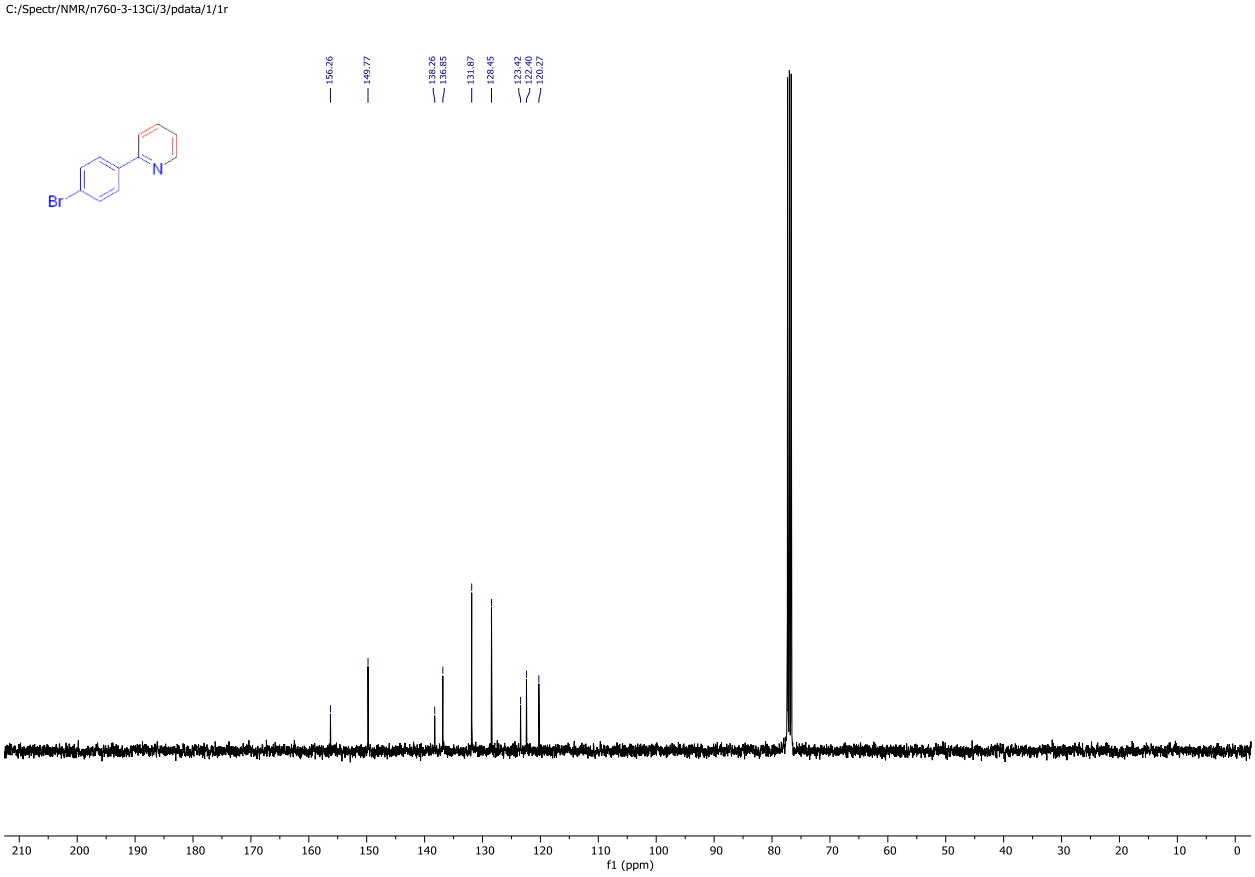
^{1}H NMR Spectrum of **2g**



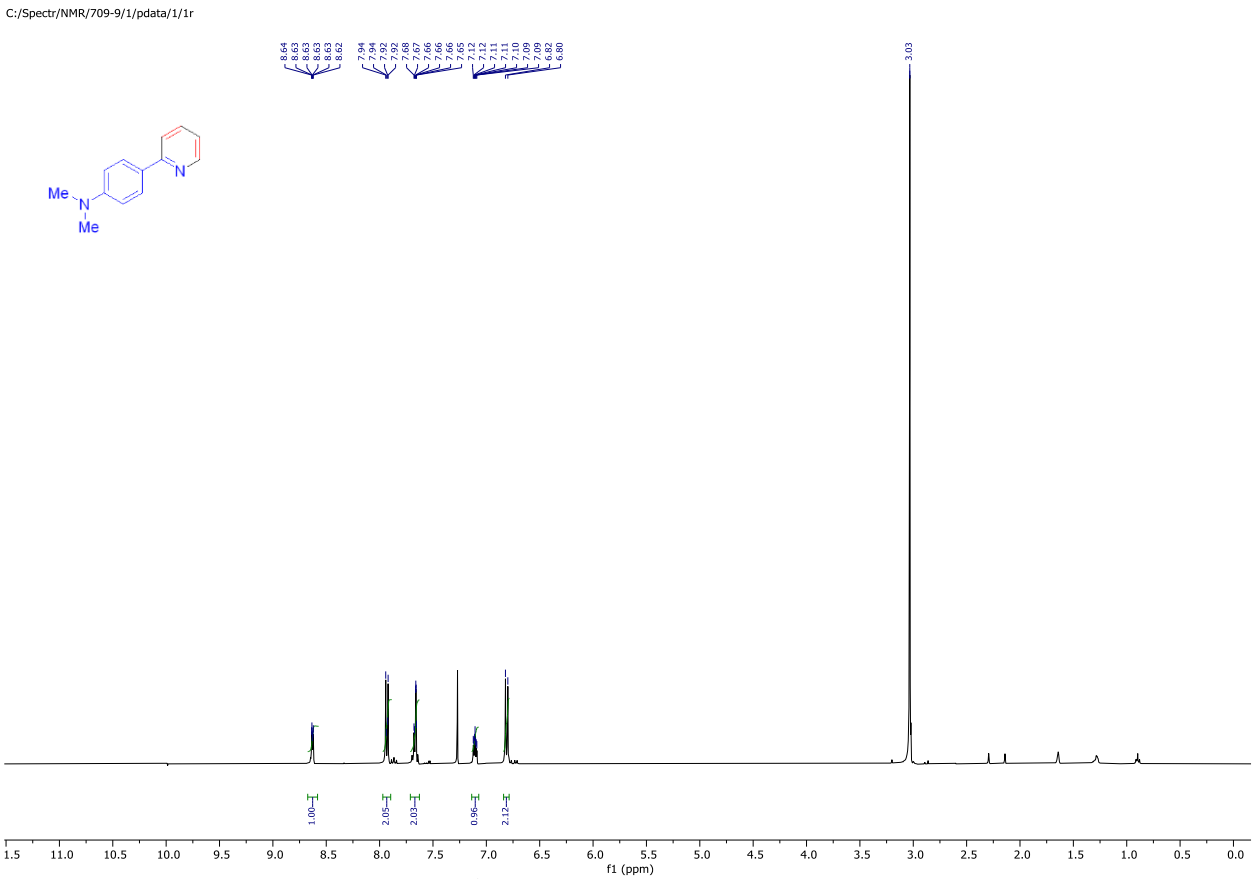
^{13}C NMR Spectrum of **2g**



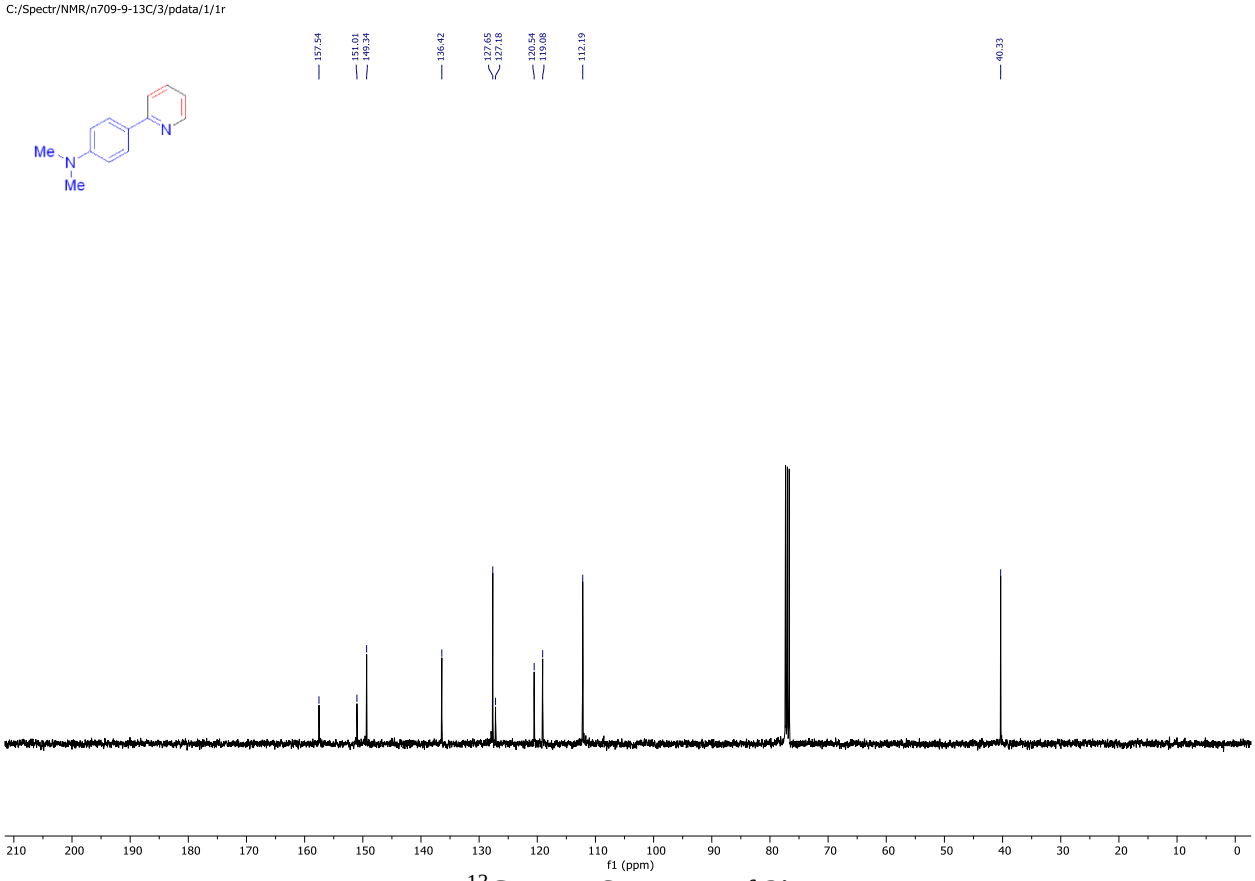
^{1}H NMR Spectrum of **2h**



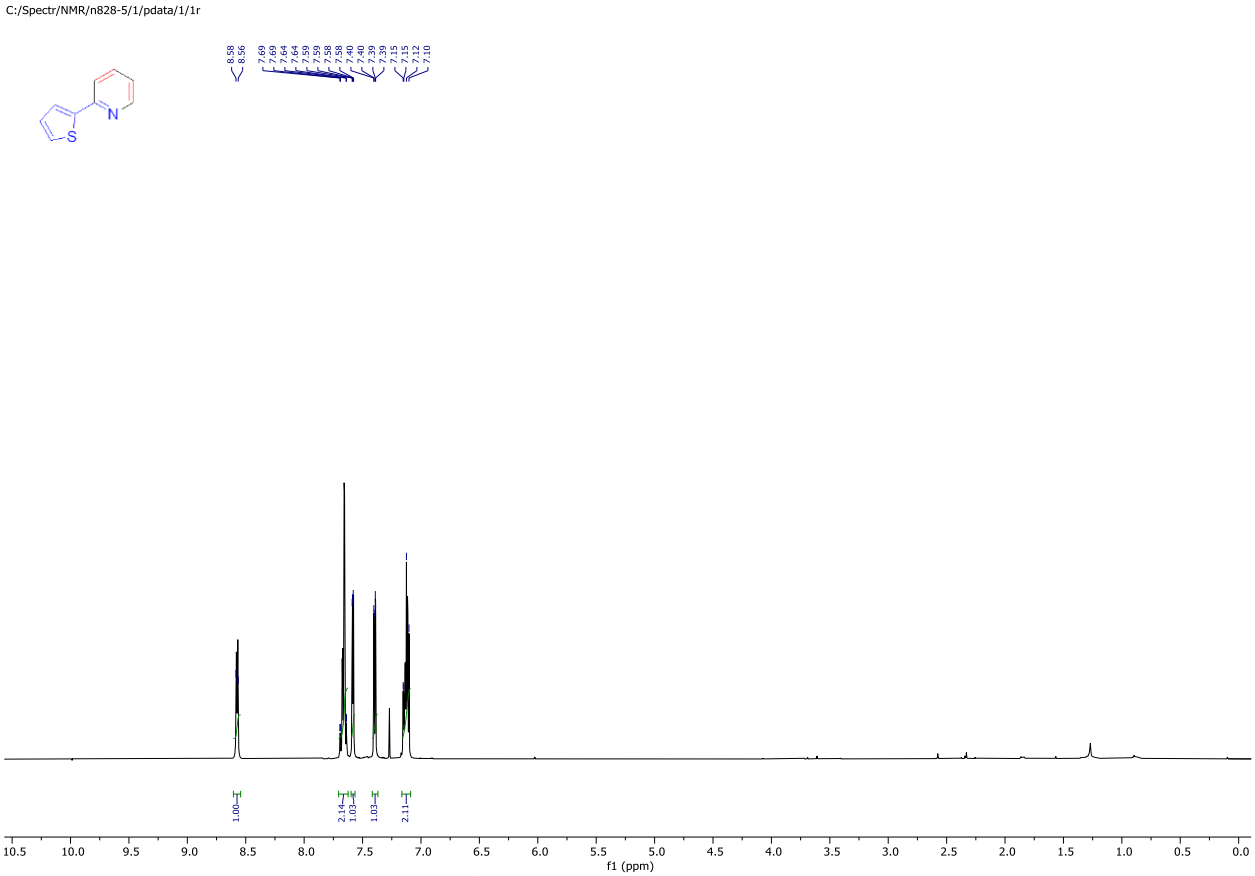
^{13}C NMR Spectrum of **2h**



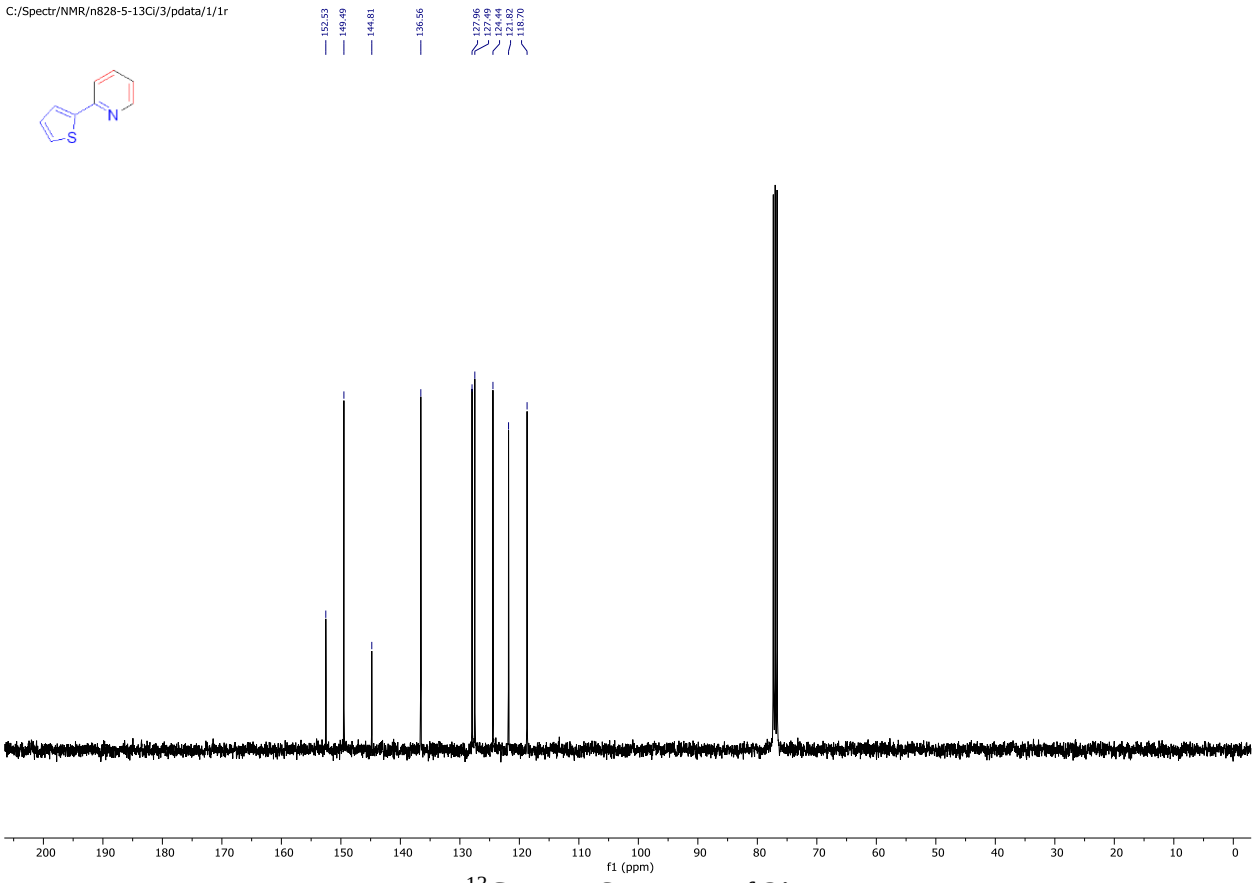
^{1}H NMR Spectrum of **2i**



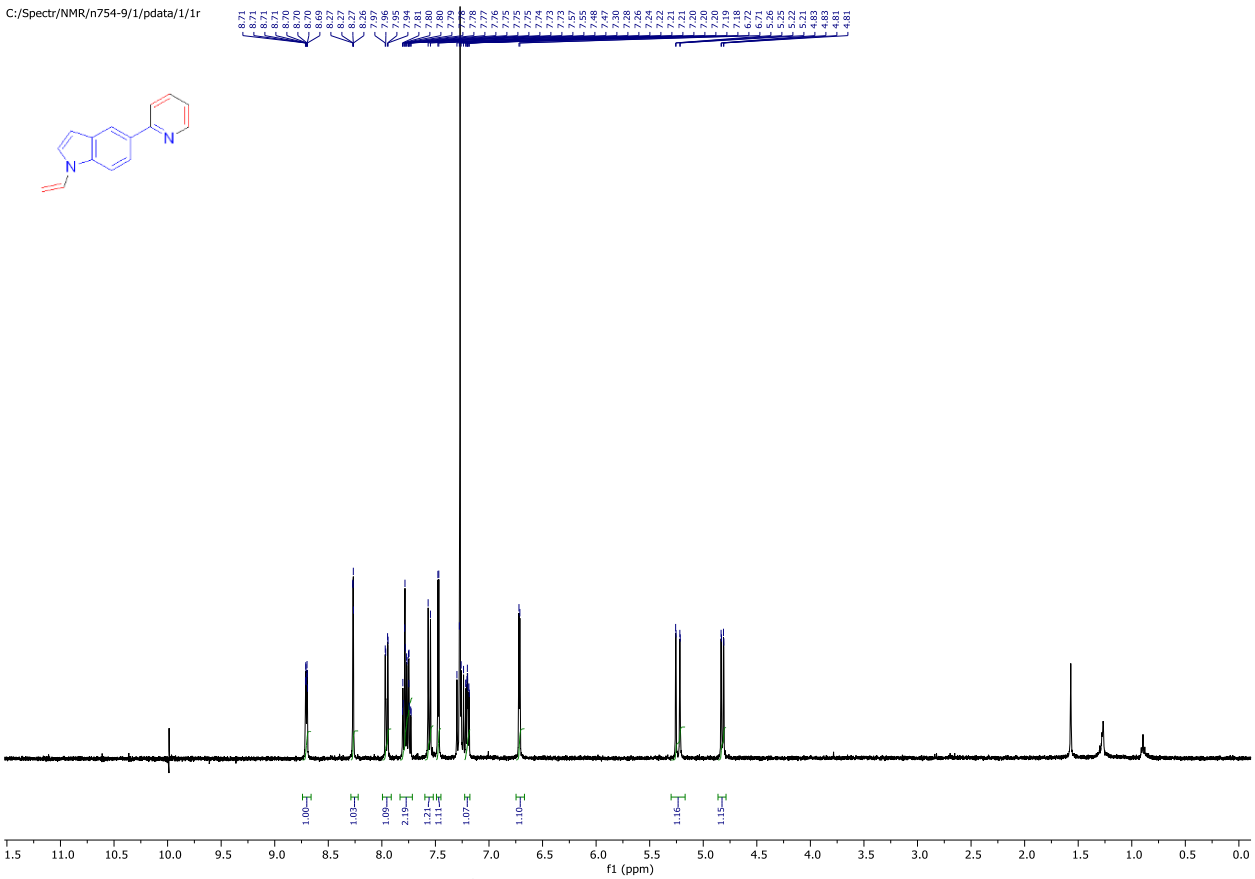
^{13}C NMR Spectrum of **2i**



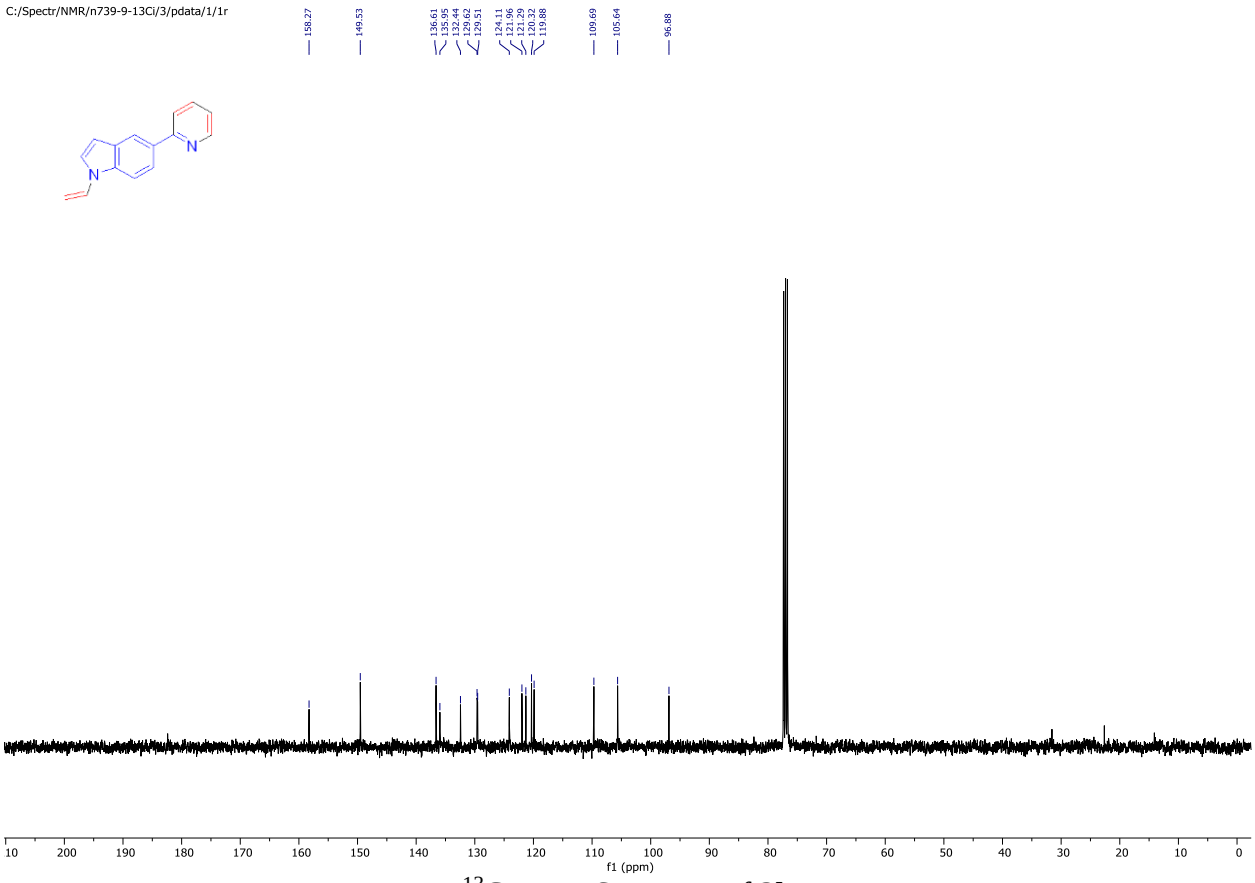
^{1}H NMR Spectrum of **2j**



^{13}C NMR Spectrum of **2j**



^{1}H NMR Spectrum of **2k**



^{13}C NMR Spectrum of **2k**

References

S1 B. Heller and G. Oehme, *J. Chem. Soc., Chem. Commun.*, 1995, 179; https://doi.org/10.1039/C39950000179.

S2 C. Liu and W. Yang, *Chem. Commun*., 2009, 6267; https://doi.org/10.1039/b912364d.

S3 Y. Wakatsuki and H. Yamazaki, *Tetrahedron Lett.*, 1973, **14**, 3383; https://doi.org/10.1016/s0040-4039(01)86920-3.

S4 M. L. N. Rao and R. J. Dhanorkar, *Eur. J. Org. Chem*. 2014, 5214; https://doi.org/10.1002/ejoc.201402455.

S5 Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Commun*., 2007, 5069; https://doi.org/10.1039/b712207a.

S6 X. Lei, Y. Wang, S. Ma and P. Jiao, *J. Org. Chem.*, 2024, **89**, 7148; https://doi.org/10.1021/acs.joc.4c00525.

S7 M. Tingoli, M. Tiecco, L. Testaferri, R. Andrenacci and R. Balducci, *J. Org. Chem*. 1993, **58**, 6097; https://doi.org/10.1021/jo00074a042o.