Mechanochemical Tuning of Pd(BIAN–NHC) Allyl/Cinnamyl Complexes for Enhanced Cross-Coupling

Electronic Supplementary Information

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1. General Information

All catalytic reactions proceeded smoothly under ambient air without requiring an inert atmosphere or energy-intensive conditions. Ball-milling experiments were conducted in a planetary mill, with operational frequencies ranging from 100 to 300 rpm, using zirconia (ZrO2) reactors (25 mL) loaded with milling bodied (Ø = 5 mm) of the same material. Unless otherwise specified, all chemicals were purchased from commercial sources and used without further purification at the highest available purity. NMR spectra (^{1}H, 400/500 MHz; ^{13}C, 101/125 MHz) were recorded at 298 K on Bruker Advance spectrometers. Chemical shifts are referenced to residual solvent signals (CDCl3: δ 7.26 ppm for 1H, δ 77.23 ppm for ^{13}C; C_6D_6: δ 7.16 ppm for 1H, δ 128.39 ppm for ^{13}C). Coupling constants (J) are reported in Hz. Signal multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

2. Synthesis of BIAN-NHC-Diimine and BIAN-NHC-HCl Salt

2.1 Synthesis of 7,9-Bis(2,6-diisopropylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium Chloride (1a)

A mixture of diimine (2.0 g) and chloromethyl ethyl ether (8 mL) in a 300 mL round-bottom flask was stirred at 100 °C for 24 h. After cooling to room temperature, diethyl ether (3 × 20 mL) was added. The resulting suspension was filtered through a porosity 3 glass frit. The crude product was triturated with anhydrous diethyl ether (3 × 20 mL) to afford the pure yellow solid (82% yield) [1].

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.11 (s, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.32–7.28 (m, 6H), 6.67 (d, JJ = 7.3 Hz, 2H), 3.09–2.85 (m, 4H), 1.89 (s, 2H) 1.31 (d, JJ = 6.8 Hz, 12H), 0.98 (d, J = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.95, 142.75, 137.56, 132.31, 130.69, 130.14, 129.17, 128.37, 125.04, 122.99, 122.98, 29.42, 24.67, 23.57.

Elemental Analysis: Calcd for $C_{37}H_{41}ClN_2$: C, 80.92; H, 7.52; Cl, 6.46; N, 5.10. Found: C, 80.99; H, 7.62; Cl, 6.58; N, 5.22.

2.2 Synthesis of 7,9-Bis-(2,4,6-tribenzhydrylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium Chloride (1b)

Diimine (1.80 g, 1.35 mmol) was placed in an oven-dried reaction vessel. Degassed chloromethyl ethyl ether (4.0 mL) was added, and complete dissolution was observed at room temperature. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the crude mixture was diluted with anhydrous diethyl ether (50 mL) and filtered through a pad of Celite (2 cm), washing with additional ether (3 × 10 mL). The crude product was purified by trituration with anhydrous diethyl ether (3 × 20 mL), affording the desired compound as a white crystalline solid (1.50 g, 80% yield)[1].

^{1}H NMR (500 MHz, $CDCl_3$): δ 12.93 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.22–6.79 (m, 46H), 6.64 (m, 12H), 6.43 (m, 8H), 6.14 (d, J = 6.9 Hz, 2H), 5.42 (s, 2H), 5.33–5.15 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.35, 142.73, 141.49, 141.09, 140.65, 137.74, 131.41, 129.82 , 129.42, 129.29, 129.26, 128.89, 128.51, 128.47, 128.09, 126.84, 126.74, 126.60, 126.50, 122.94, 122.08, 56.28, 51.70. .

Elemental Analysis: Calcd for $C_{103}H_{77}ClN_2$: C, 89.76; H, 5.63; Cl, 2.57; N, 2.03. Found: C, 89.87; H, 5.23; Cl, 2.67; N, 2.13.

2.3 Synthesis of 7,9-Bis(2,6-dibenzhydryl-4-methylphenyl)-7H-acenaphtho[1,2-d]imidazol-9-ium Chloride (1c)

Diimine (1.80 g, 1.35 mmol) was placed in an oven-dried reaction vessel. Degassed chloromethyl ethyl ether (4.0 mL) was added, and complete dissolution was observed at room temperature. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the crude mixture was diluted with anhydrous diethyl ether (50 mL) and filtered through a pad of Celite (2 cm), washing with additional ether (3 × 10 mL). The crude product was purified by trituration with anhydrous diethyl ether (3 × 20 mL), affording the desired compound as a white crystalline solid (1.50 g, 80% yield) [2].

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.36 (s, 1H), 7.60 (dd, J = 8.2, 4.0 Hz, 2H), 7.20–6.69 (m, 40H), 6.69–6.62 (m, 6H), 6.59 (s, 4H), 6.23 (d, J = 7.0 Hz, 2H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 142.88, 141.83, 141.62, 141.08, 140.69, 137.85, 130.86, 129.57, 129.46, 129.41, 129.25, 129.05, 128.60, 128.39, 128.20, 126.90, 126.76, 123.20, 121.93, 21.98.
Elemental Analysis: Calcd for $C_{79}H_{61}ClN_2$: C, 88.36; H, 5.73; Cl, 3.30; N, 2.61. Found: C, 88.46; H, 5.83; Cl, 3.45; N, 2.72.

3. General Procedure for the Synthesis of Novel Catalysts

3.1 Synthesis of [Pd(BIAN-IPr)Cl(Allyl)] Complex (2a)

A 4 mL vial equipped with a magnetic stirring bar was charged with BIAN-IPr·HCl **(1a)** (261 mg, 0.47 mmol, 2.0 equiv.) and K_2CO_3 (130 mg, 0.97 mmol, 4.0 equiv.) in acetone (2 mL). The mixture was stirred at room temperature for 15 min. [Pd(allyl)(μ-Cl)]$_2$ (86.4 mg, 0.235 mmol, 1.0 equiv.) was added, and stirring was continued for 1 h. The solvent was removed under reduced pressure. The residue was dissolved in DCM, filtered through a silica gel/Celite pad, and eluted with DCM. After concentration *in* vacuum, the product was precipitated with n-hexane and isolated by decantation. Drying under high vacuum afforded the pure complex as an orange-yellow powder (96% yield) [2-4].

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.57 (m, 2H), 7.41 (d, J = 7.8 Hz, 4H), 7.33 (m, 2H), 6.86 (d, J = 7.0 Hz, 2H), 5.32 (s, 1H), 4.94 (m, 1H), 4.00 (d, J = 7.2 Hz, 2H), 3.37 (dt, J = 13.3, 6.6 Hz, 2H), 3.30 (d, J = 5.4 Hz, 1H), 3.16 (m, 2H), 2.93 (d, J = 13.4 Hz, 1H), 1.89 (d, J = 11.8 Hz, 1H), 1.40 (d, J = 6.0 Hz, 12H), 0.99 (d, J = 6.7 Hz, 12H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 193.00, 146.41, 146.25, 140.37, 134.67, 134.67, 130.22, 129.92, 129.66, 127.78, 127.31, 126.30, 124.45, 124.19, 121.61, 114.47, 114.47, 53.42, 50.29, 28.71, 28.69, 25.82, 25.47, 23.83, 23.32.
Elemental Analysis: Calcd for $C_{41}H_{52}ClN_2Pd$: C, 68.90; H, 7.33; Cl, 4.96; N, 3.92; Pd, 14.89. Found: C, 68.98; H, 7.44; Cl, 4.99; N, 3.98; Pd, 14.96.

3.2 Synthesis of [Pd(BIAN-IPr*)Cl(Allyl)] Complex (2b)

A 4 mL vial equipped with a magnetic stirring bar was charged with BIAN-IPr*·HCl **(1c)** (647 mg, 0.47 mmol, 2.0 equiv.) and K_2CO_3 (130 mg, 0.97 mmol, 4.0 equiv.) in acetone (2 mL). The mixture was stirred at room temperature for 15 min. [Pd(allyl)(μ-Cl)]$_2$ (86.4 mg, 0.235 mmol, 1.0 equiv.)

was added, and stirring was continued for 1 h. The mixture was worked up as described for **2a**. The pure complex was obtained as an orange powder (97% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 – 7.05 (m, 22H), 6.86 – 6.43 (m, 28H), 6.21 (s, 2H), 5.95 (s, 2H), 5.65 (d, J = 6.8 Hz, 2H), 5.37 (s, 1H), 4.61 – 4.57 (m, 1H), 2.41 (s, 6H), 0.90 (d, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.11, 143.84, 140.52, 138.53, 135.54, 130.39, 129.57, 127.67, 126.06, 125.51, 124.71, 121.42, 114.74, 72.64, 53.17, 51.66, 21.95.
Elemental Analysis: Calcd. for $C_{83}H_{72}ClN_2Pd$: C, 80.44; H, 5.86; Cl, 2.86; N, 2.26; Pd, 8.59. Found: C, 80.56; H, 5.78; Cl, 2.96; N, 2.36; Pd, 8.67.

3.3 Synthesis of [Pd(BIAN-IPr$^{\#}$)Cl(cinnamyl)] Complex (2c)

A 4 mL vial equipped with a magnetic stirring bar was charged with BIAN-IPr$^{\#}$·HCl **(1b)** (647 mg, 0.47 mmol, 2.0 equiv.) and K_2CO_3 (130 mg, 0.97 mmol, 4.0 equiv.) in acetone (2 mL). The mixture was stirred at room temperature for 15 min. [Pd(cinnamyl)(μ-Cl)]$_2$ (122 mg, 0.235 mmol, 1.0 equiv.) was added, and stirring was continued for 1 h. The mixture was worked up as described for **2a**. The pure complex was obtained as an orange powder (97% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 5H), 7.29 (s, 4H), 7.08 (m, 44H), 6.61 (m, 22H), 6.06 (s, 4H), 5.66 (d, J = 9.7 Hz, 2H), 5.57 (s, 2H), 4.89 (m, 1H), 4.47 (d, J = 14.7 Hz, 1H), 0.91 (t, J = 6.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.44 (m, 0H), 144.39, 143.47, 143.38, 142.29, 141.72, 140.63, 138.19, 135.86, 131.14, 130.13 , 129.32, 128.69, 128.39, 127.79, 127.72, 127.65, 126.38, 126.08, 126.04, 125.99, 125.65, 124.82, 121.32, 109.01, 56.45, 51.5, 49.22.
Elemental Analysis: Calcd for $C_{113}H_{92}ClN_2Pd$: C, 83.79; H, 5.72; Cl, 2.19; N, 1.73; Pd, 6.57. Found: C, 83.99; H, 5.72; Cl, 2.23; N, 1.73; Pd, 6.64.

3.4 Synthesis of [Pd(BIAN-IPr$^{\#}$)Cl(Allyl)] Complex (2d)

A 4 mL vial equipped with a magnetic stirring bar was charged with BIAN-IPr$^{\#}$·HCl **(1b)** (647 mg, 0.47 mmol, 2.0 equiv.) and K_2CO_3 (130 mg, 0.97 mmol, 4.0 equiv.) in acetone (2 mL). The mixture was stirred at room temperature for 15 min. [Pd(allyl)(μ-Cl)]2 (86.4 mg, 0.235 mmol, 1.0 equiv.) was added, and stirring was continued for 1 h. The mixture was worked up as described for **2a**. The pure complex was obtained as an orange powder (97% yield)[2].

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (m, 46H), 6.60 (m, 20H), 6.48 (s, 2H), 6.00 (d, J = 60.1 Hz, 4H), 5.65 (d, J = 6.9 Hz, 2H), 5.55 (s, 2H), 4.41 (m, 1H), 4.10 (d, J = 7.0 Hz, 1H), 2.96 (d, J = 7.7 Hz, 1H), 2.36 (s, 1H), 0.89 (d, J = 10.2 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.36, 144.46, 143.33, 141.61, 140.39, 135.84, 131.13, 130.11, 129.26, 128.34, 127.69, 126.38, 126.03, 125.96, 125.68, 124.73, 121.31, 114.59, 56.46, 53.32, 51.72.

Elemental Analysis: Calcd for $C_{107}H_{88}ClN_2Pd$: C, 83.25; H, 5.75; Cl, 2.30; N, 1.81; Pd, 6.89. Found: C, 83.37; H, 5.95; Cl, 2.45; N, 1.94; Pd, 6.98.

4. General Procedure for mechanochemical Suzuki-Miyaura Cross-Coupling of Aryl Chlorides

Aryl chloride (1.0 equiv., 0.5 mmol), aryl boronic acid (1.1 equiv., 0.55 mmol), K_2CO_3 (1.5 equiv., 0.75 mmol), catalyst [Pd(IPr$^{\#}$)(cinnamyl)Cl] **(2c)** (0.125-0.062 mol%), with 10 ZrO_2 ball (ø= 5mm) were placed in a 25 mL zirconia vessel containing (EtOH 0.2μL/mg) as liquid assisted grinding agent, ground at room temperature with 300 rpm speed for 30 minutes. The mixture was diluted with DCM (10 mL), and reaction quenched with petroleum ether. The conversion was checked by GC analysis and further purification and isolation of product done by flash chromatography on silica gel (EtOAc/petroleum ether) to afford the product[10].

4.1 Synthesis of 4-Methoxy-1,1'-biphenyl (3a)

Eluent: EtOAc:PE = 1:10. White solid (96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 4H), 7.46–7.39 (m, 2H), 7.34–7.28 (m, 1H), 7.02–6.96 (m, 2H), 3.86 (s, 3H) [3].

4.2 Synthesis of 4-Methyl-1,1'-biphenyl (3b)

Eluent: EtOAc:PE = 1:8. White solid (96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.3 Hz, 1H), 7.26 (m, 2H), 2.41 (s, 3H) [3].

4.3 Synthesis of 4-(Trifluoromethyl)-1,1'-biphenyl (3c)

Eluent: EtOAc:PE = 1:7. White solid (99% yield) .

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 4H), 7.60 (m, 2H), 7.48 (d, J = 6.3, 4.1, 1.0 Hz, 2H), 7.43 (dd, J = 5.0, 3.6 Hz, 1H)[3,5] .

4.4 Synthesis of 3-Phenylpyridine (3d)

Reaction conducted at 50 °C. Eluent: EtOAc:PE = 1:4. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, J = 1.9 Hz, 1H), 8.60 (d, J = 4.8, 1.5 Hz, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.59 (m, 2H), 7.41 (m, 4H) [3, 6].

4.5 Synthesis of 4-Methoxy-4'-methyl-1,1'-biphenyl (3e)

Eluent: EtOAc:PE = 1:7. White solid (96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.9 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 3H) [7].

4.6 Synthesis of 1,1'-Biphenyl (3f)

Eluent: EtOAc:PE = 1:9. White solid (99% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.1 Hz, 4H), 7.45 (t, J = 7.5 Hz, 4H), 7.35 (t, J = 7.4 Hz, 2H) [3].

4.7 Synthesis of 4,4'-Dimethyl-1,1'-biphenyl (3g)

Eluent: EtOAc:PE = 1:6. White solid (96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.0 Hz, 4H), 7.25 (d, J = 7.7 Hz, 4H), 2.38 (s, 6H) [4].

4.8 Synthesis of 4-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (3h)

Eluent: EtOAc:PE = 1:8. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 4H), 2.41 (s, 3H) [8].

4.9 Synthesis of 4-Fluoro-4'-methoxy-1,1'-biphenyl (3i)

Eluent: EtOAc:PE = 1:10. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 4H), 7.10 (t, J = 8.7 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H) [9].

4.10 Synthesis of 4-Fluoro-4'-methyl-1,1'-biphenyl (3j)

Eluent: EtOAc:PE = 1:20. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (m, 4H), 7.22–7.06 (m, 4H), 2.39 (s, 3H) [9].

4.11 Synthesis of 4,4'-Dimethoxy-1,1'-biphenyl (3k)

Eluent: EtOAc:PE = 1:9. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.07 (m, 4H), 7.04 – 6.73 (m, 4H), 3.77 (s, 6H) [9].

4.12 Synthesis of [1,1'-Biphenyl]-4-carbaldehyde (3l)

Eluent: EtOAc:PE = 1:12. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.96 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.64 (m, 2H), 7.49 (m, 2H), 7.43 (m, 1H) [3].

4.13 Synthesis of 1-([1,1'-Biphenyl]-4-yl)ethanone (3m)

Eluent: EtOAc:PE = 1:12. White solid (92% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.6 Hz, 2H), 7.69 (m, 2H), 7.63 (m, 2H), 7.48 (m, 2H), 7.42 (m, 1H), 2.64 (s, 3H) [3].

4.14 Synthesis of 4-(Naphthalen-2-yl)benzaldehyde (3n)

Eluent: EtOAc:PE = 1:7. White solid (89% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.11 (s, 1H), 7.97–7.89 (m, 7H), 7.55 (d, J = 8.3 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H).

4.15 Synthesis of 1-(4-(Naphthalen-2-yl)phenyl)ethanone (3o)

Eluent: EtOAc:PE = 1:8. White solid (91% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 3H), 7.95 (m, 6H), 7.46 (m, 2H), 2.69 (s, 3H).

4.16 Synthesis of 3-(Naphthalen-2-yl)pyridine (3p)

Reaction conducted at 50 °C. Eluent: EtOAc:PE = 1:6. White solid (89% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.99 (d, *J* = 1.8 Hz, 1H), 8.63 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.05 (d, *J* = 1.3 Hz, 1H), 8.02 – 7.99 (m, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.73 – 7.70 (m, 1H), 7.55 – 7.51 (m, 2H), 7.43 – 7.40 (m, 1H).

4.17 Synthesis of 4-(7-Methoxynaphthalen-2-yl)benzaldehyde (3q)

Eluent: EtOAc:PE = 1:8. White solid (86% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 10.04 (s, 1H), 7.92 (d, J = 7.4 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.93 (m, 4H), 3.86 (s, 3H).

4.18 Synthesis of 3-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3r)

Eluent: EtOAc:PE = 1:7. White solid (93% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.73 (m, 4H), 7.24 (d, J = 8.1 Hz, 1H), 7.19 (m, 2H), 7.01 (d, J = 7.7 Hz, 1H), 3.86 (s, 3H).

4.19 Synthesis of 1-(p-Tolyl)naphthalene (3s)

Eluent: EtOAc:PE = 1:10. White solid (91% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88–7.54 (m, 7H), 7.44 (d, J = 8.4, 9.3 Hz, 4H), 2.40 (s, 3H).

5. General Procedure for mechanochemical Buchwald-Hartwig Amination Reaction

A 25 mL zirconia vessel was charged with the catalyst [Pd(NHC)Cl(Cinnamyl)] (0.125 mol%), aryl chloride (0.50 mmol), amine (0.55 mmol), K^{t}BuO (0.75 mmol), (EtOH 0.2µL/mg) as liquid assisted grinding agent, with 10 ZrO_2 ball (ø= 5mm) ground at room temprature with 300 rpm speed for 40-60minutes. The mixture was diluted with DCM (10 mL), and reaction quenched with diethylether. The conversion was checked by GC analysis and further purification and isolation of product done by flash chromatography on silica gel (EtOAc/petroleum ether) to afford the product[11,12].

5.1 Synthesis of 4-(4-Methoxyphenyl)morpholine (4a)

Eluent: EtOAc:PE = 1:5. White solid (99% yield).

^{1}H NMR (400 MHz, CDCl$_3$): ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.91 – 6.83 (m, 4H), 3.88 – 3.84 (m, 4H), 3.77 (s, 3H), 3.07 – 3.04 (m, 4H). [3]

5.2 Synthesis of 4-Methoxy-N-phenylaniline (4b)

Eluent: EtOAc:PE = 1:7. White solid (90% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19 (m, 2H), 7.06 (m, 2H), 6.92–6.78 (m, 5H), 5.47 (s, 1H), 3.78 (s, 3H) [3].

5.3 Synthesis of 4-(4-(Trifluoromethyl)phenyl)morpholine (4c)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 3.95–3.81 (m, 4H), 3.29–3.15 (m, 4H) [3].

5.4 Synthesis of N-Phenyl-4-(trifluoromethyl)aniline (4d)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.14 (m, 4H), 6.73 (m, 5H), 3.24 (s, 1H).

5.5 Synthesis of 4-(p-Tolyl)morpholine (4e)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.09 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 5.6 Hz, 2H), 4.10–3.66 (m, 4H), 3.31–2.92 (m, 4H), 2.27 (s, 3H) [3].

5.6 Synthesis of 4-Methoxy-N-methyl-N-phenylaniline (4f)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (m, 2H), 7.06 (t, *J* = 13.5 Hz, 2H), 6.85 (m, 5H), 3.80 (s, 3H), 3.28 (m, 3H) [3].

5.7 Synthesis of N-Methyl-N-phenylpyridin-3-amine (4g)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (d, J = 2.8 Hz, 1H), 8.11 (d, J = 4.6 Hz, 1H), 7.43–7.25 (m, 2H), 7.21–7.01 (m, 5H), 3.35–3.26 (m, 3H) [3].

5.8 Synthesis of Bis(4-methoxyphenyl)amine (4h)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (m, 8H), 3.69 (s, 6H), 1.58 (s, 1H) .

5.9 Synthesis of 3-Methoxy-N-phenylaniline (4i)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–6.95 (m, 5H), 6.86–6.82 (m, 4H), 5.39 (s, 1H), 3.78 (s, 3H) [3].

5.10 Synthesis of 2,6-Diethyl-N-phenylaniline (4j)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (m, 5H), 6.40 (m, 3H), 5.06 (s, 1H), 2.57 (dd, J = 6.4, 1.1 Hz, 4H), 2.22 (s, 6H).

5.11 Synthesis of 2,4,6-Trimethyl-N-(p-tolyl)aniline (4k)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 10.7, 2.8 Hz, 4H), 6.42 – 6.38 (m, 2H), 5.23 (s, 1H), 2.29 (s, 3H), 2.22 (s, 3H), 2.15 (s, 6H).

5.12 Synthesis of N-(4-Methoxyphenyl)-2,4,6-trimethylaniline (4l)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 6.75 – 6.71 (m, 2H), 6.49 (dd, *J* = 26.0, 5.7 Hz, 2H), 5.29 (s, 1H), 3.73 (s, 3H), 2.29 (s, 3H), 2.15 (s, 6H).

5.13 Synthesis of N-Cyclohexyl-4-methoxyaniline (4m)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 – 6.74 (m, 2H), 6.60 – 6.56 (m, 2H), 3.74 (s, 3H), 2.92 (s, 1H), 2.06 – 2.01 (m, 2H), 1.78 – 1.72 (m, 2H), 1.66 – 1.61 (m, 1H), 1.46 – 1.3 (m, 2H), 1.29-1.5 (m, 2H), 1.5-0.98(m, 2H).

5.14 Synthesis of N-Cyclohexylpyridin-3-amine (4n)

Eluent: EtOAc:PE = 1:20. White solid (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.8 Hz, 1H), 7.90 (d, *J* = 4.6 Hz, 1H), 7.05 (dd, *J* =

8.3, 4.6 Hz, 1H), 6.87 – 6.83 (m, 1H), 3.61 (s, 1H), 2.06 – 2.02 (m, 2H), 1.81 – 1.74 (m, 2H), 1.69 – 1.63 (m, 1H), 1.44 – 1.10 (m, 6H).

6. Reference

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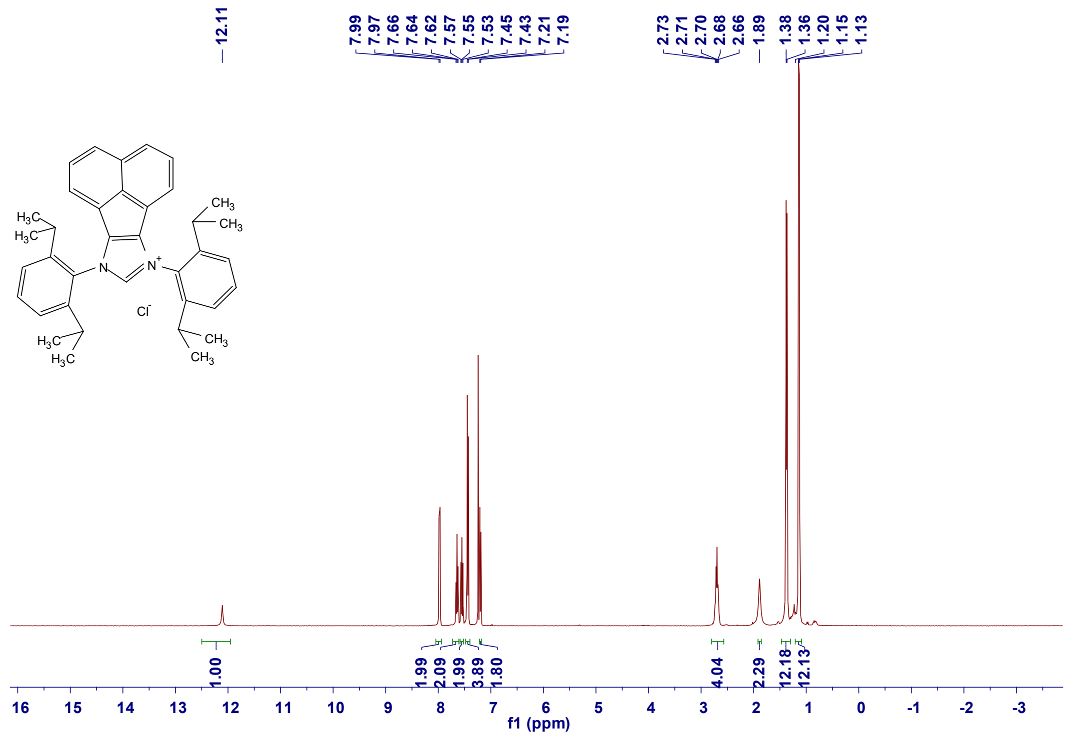
NMR Spectra

1a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7.66
7.64
7.62
7.57
7.55
7.53
7.45
7.43
7.21
7.19
2.73
2.71
2.70
2.68
2.66
1.89
1.38
1.36
1.20
1.15
1.13
1.00
1.99
2.09
1.99
3.89
1.80
4.04
2.29
12.18
12.13
16
15
14
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12
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8
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2
1
0
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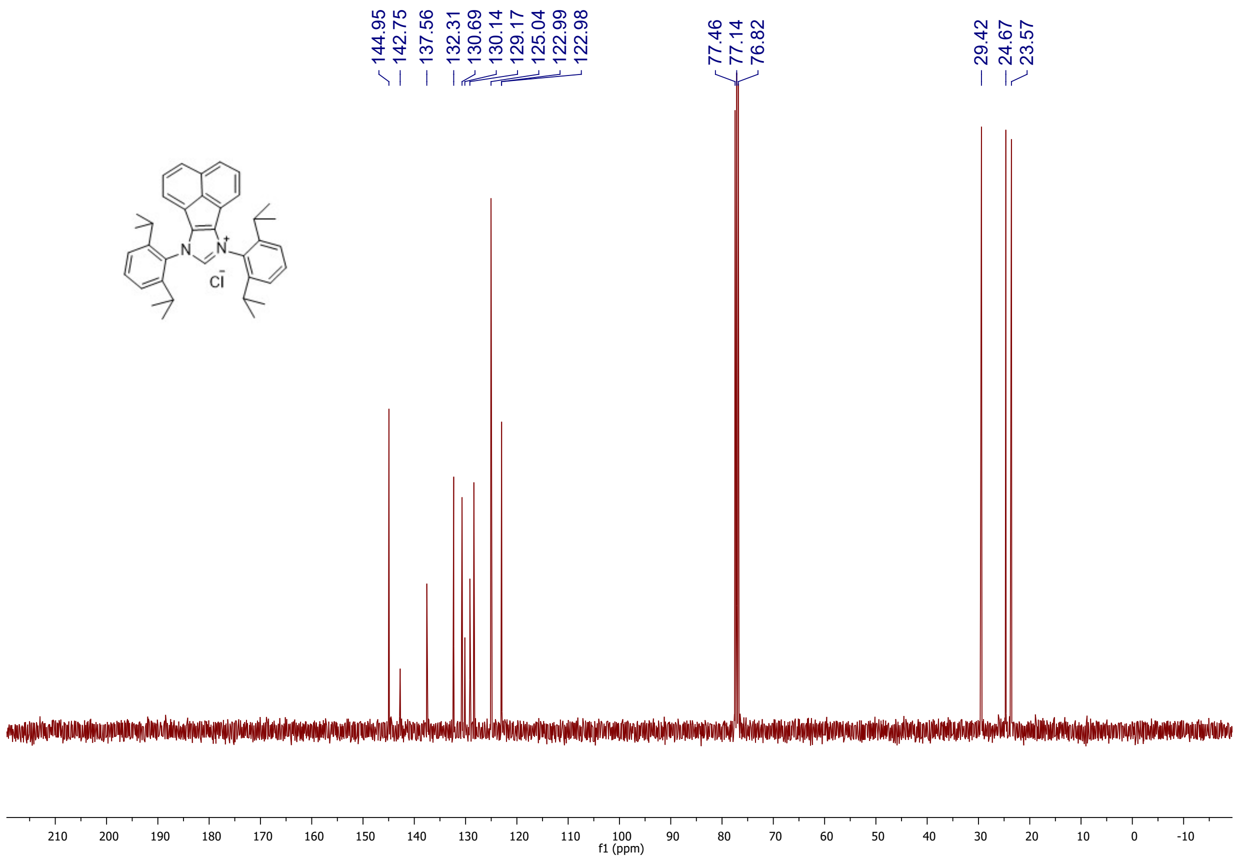
-2
-3
f1 (ppm)



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130.14
129.17
125.04
122.99
122.98
77.46
77.14
76.82
29.42
24.67
23.57
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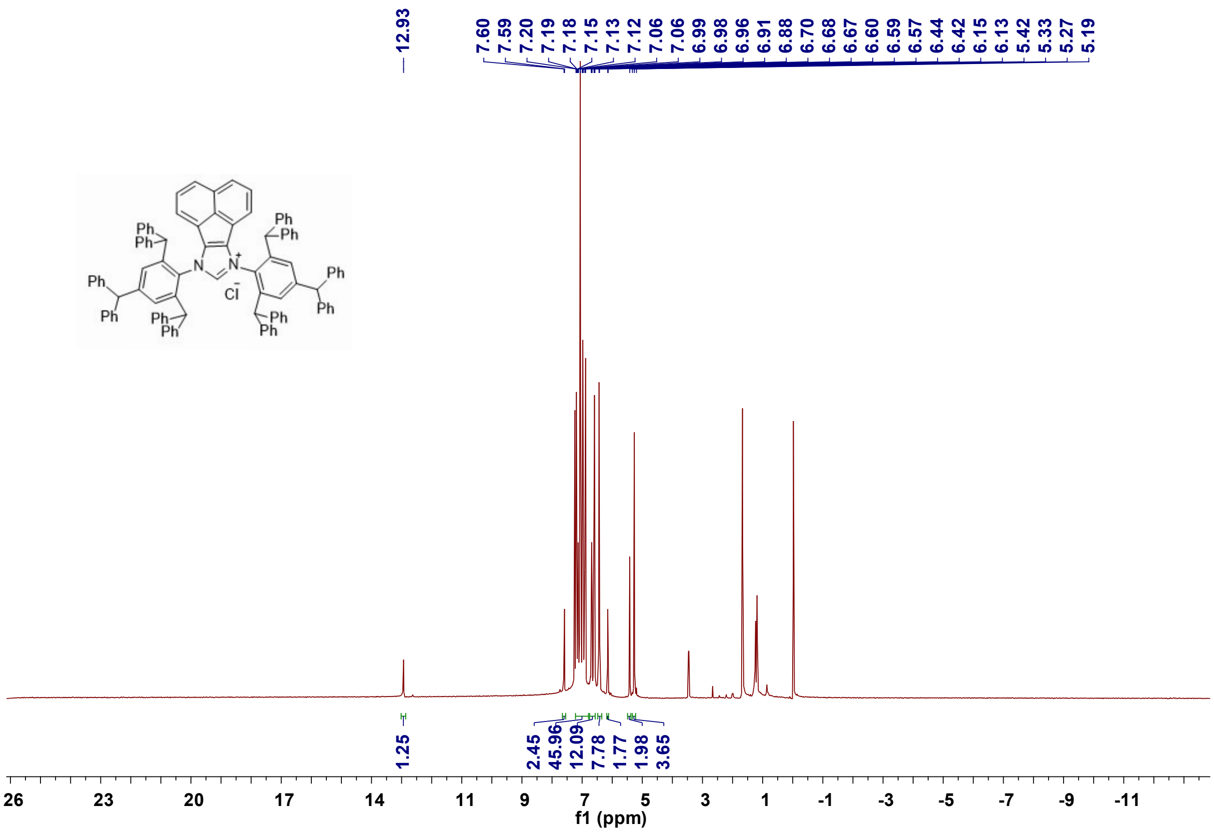
N+
Cl−
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1b



12.93
7.60 7.59 7.20 7.19 7.18 7.15 7.13 7.12 7.06 7.06 6.99 6.98 6.96 6.91 6.88 6.70 6.68 6.67 6.60 6.59 6.57 6.44 6.42 6.15 6.13 5.42 5.33 5.27 5.19
1.25
2.45 45.96 12.09 7.78 1.77 1.98 3.65
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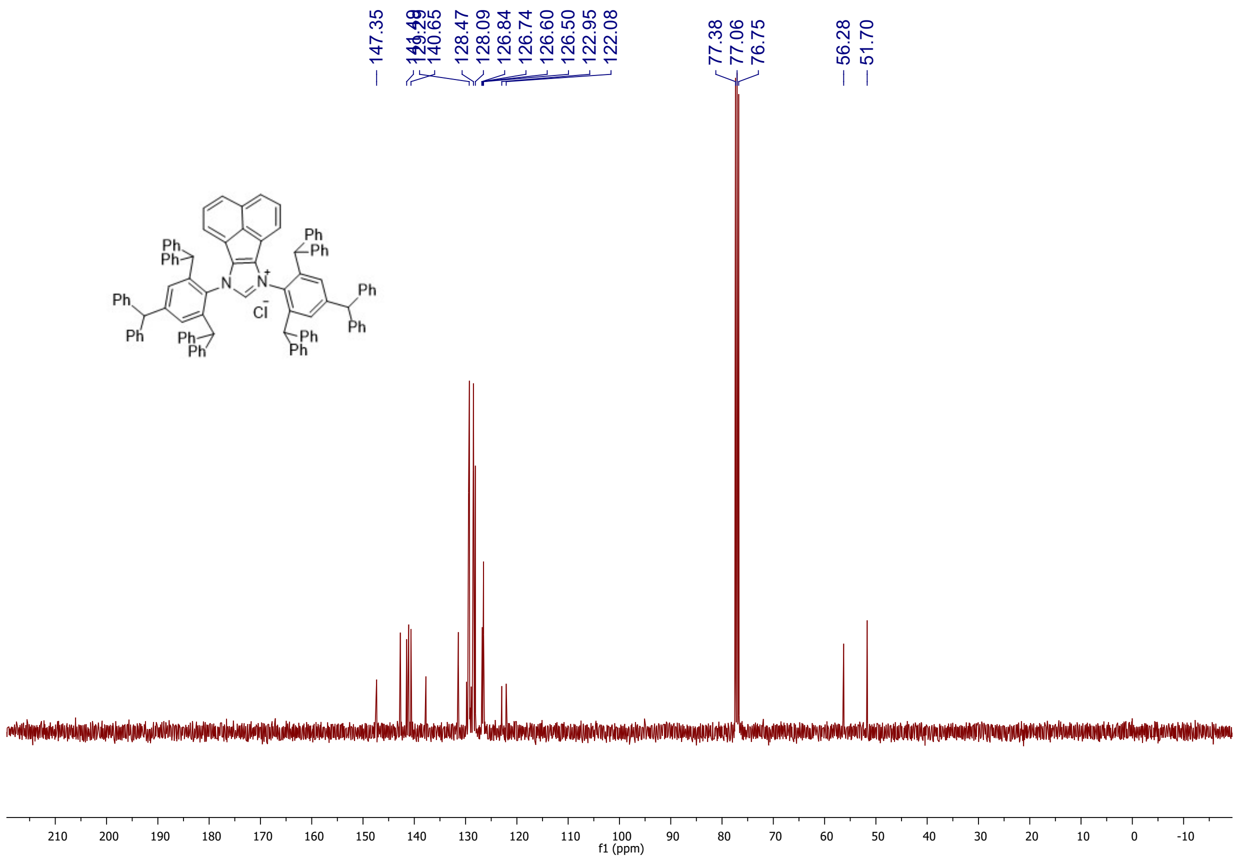
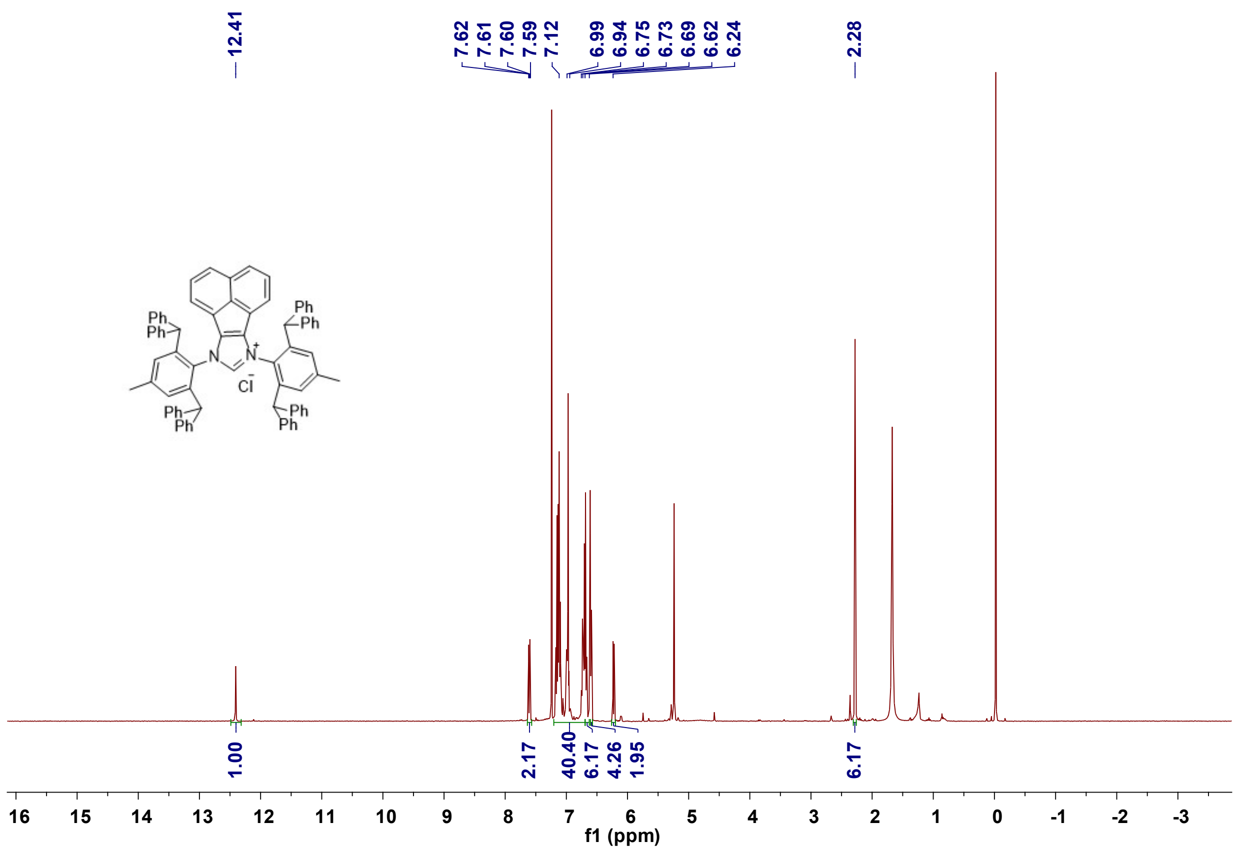
f1 (ppm)



1c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6.73
6.69
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6.24
2.28
Ph
Ph
N
N+
Cl-
1.00
2.17
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4.26
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6.17
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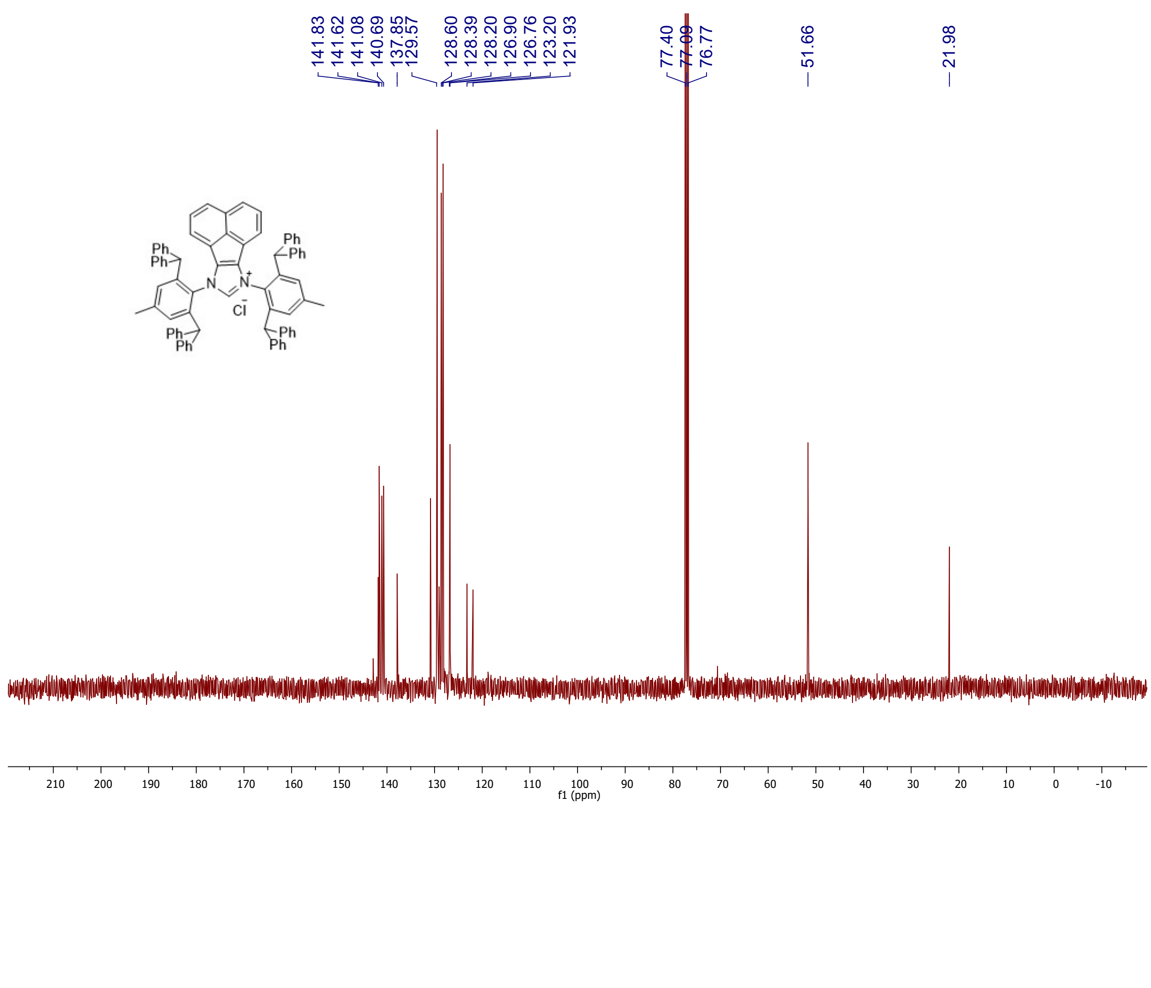
f1 (ppm)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121.93
77.40
77.09
76.77
51.66
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Ph
Ph
N
N+
Cl-
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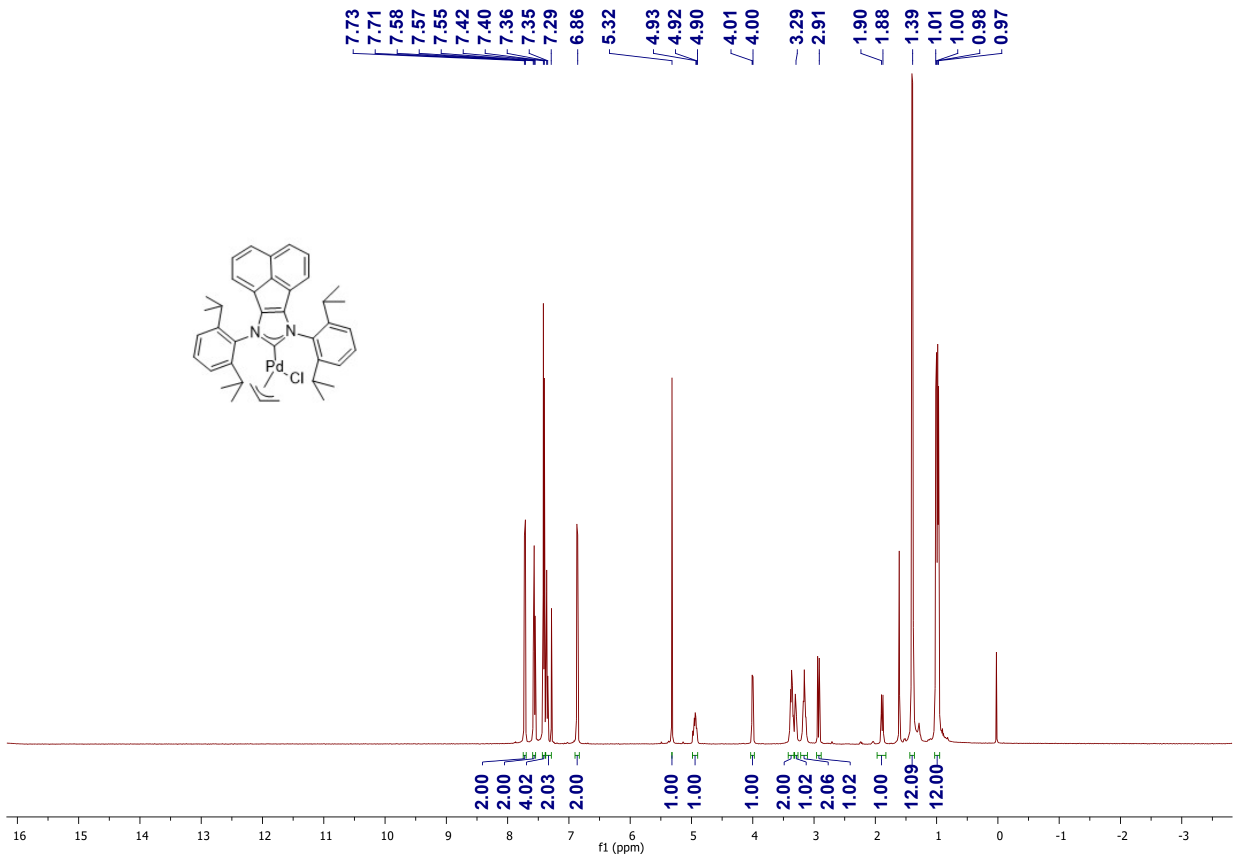
f1 (ppm)

2a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Pd
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5.32
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1.00
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2.00
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16
15
14
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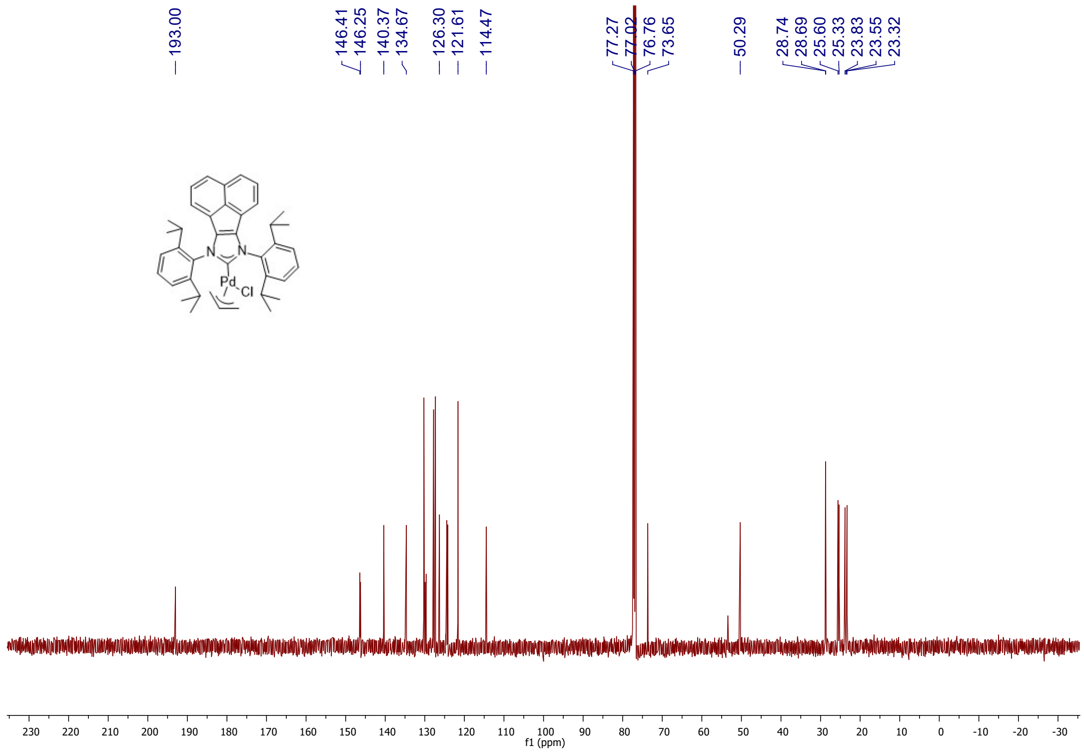
f1 (ppm)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28.74
28.69
25.60
25.33
23.83
23.55
23.32
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N
Pd
Cl
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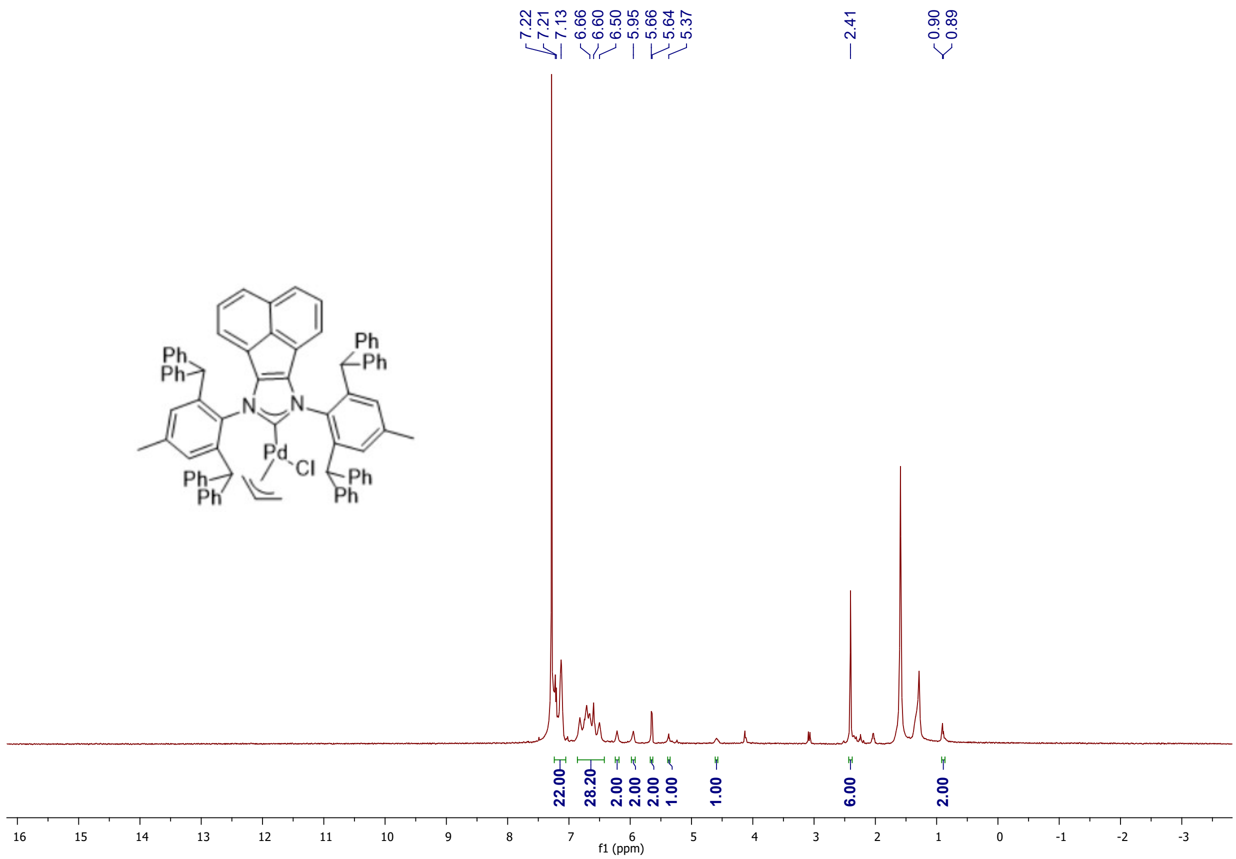
f1 (ppm)

2b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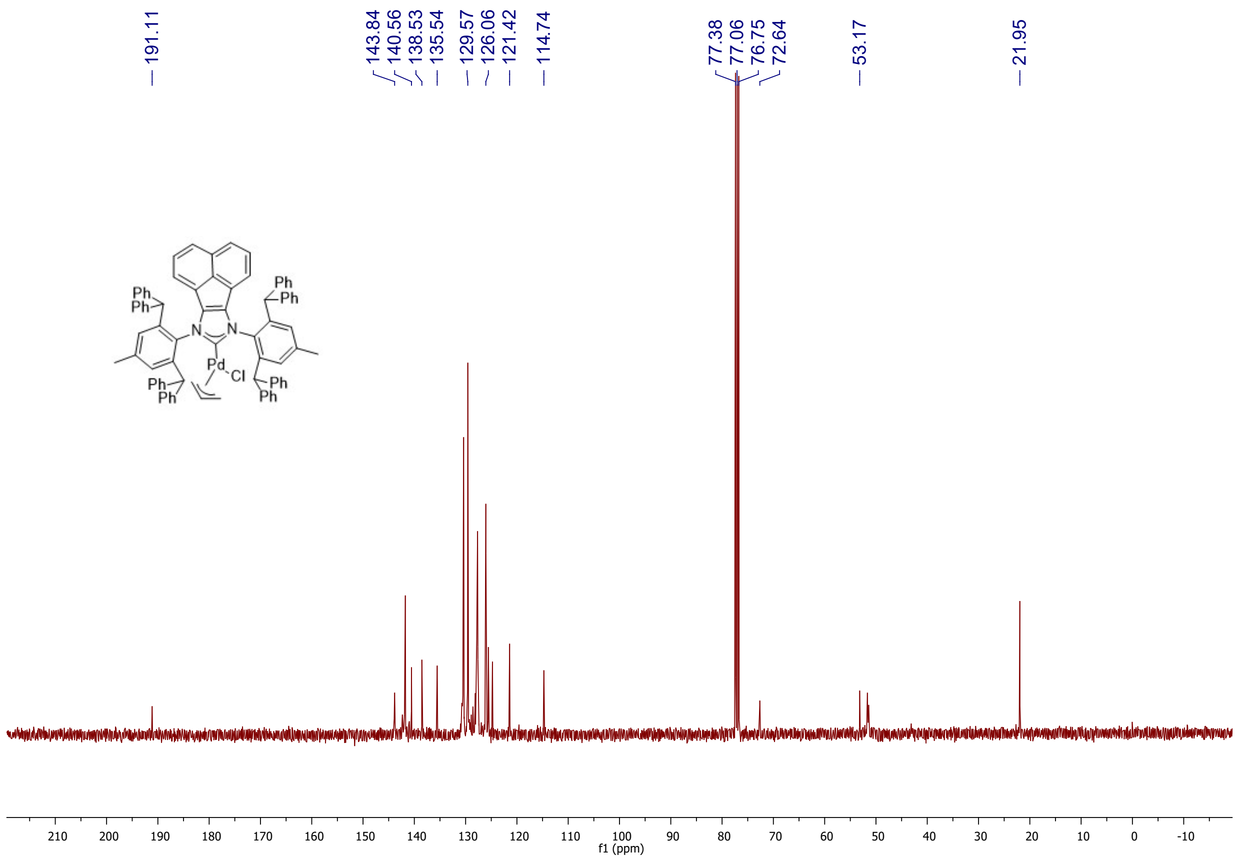
f1 (ppm)
Ph
Pd
Cl
N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Ph
Ph
Ph
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Ph
Ph
Ph
Ph
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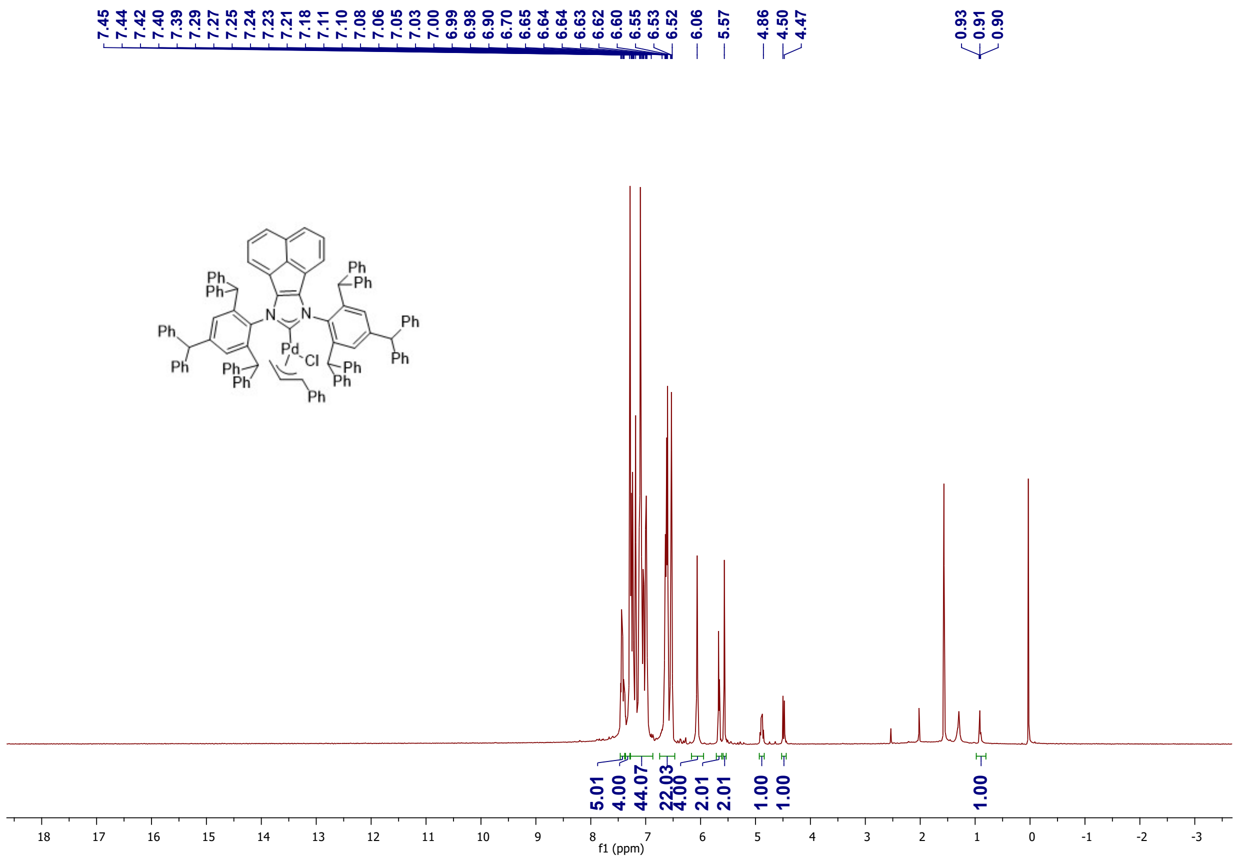
f1 (ppm)

2c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Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
Ph
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N
Pd
Cl
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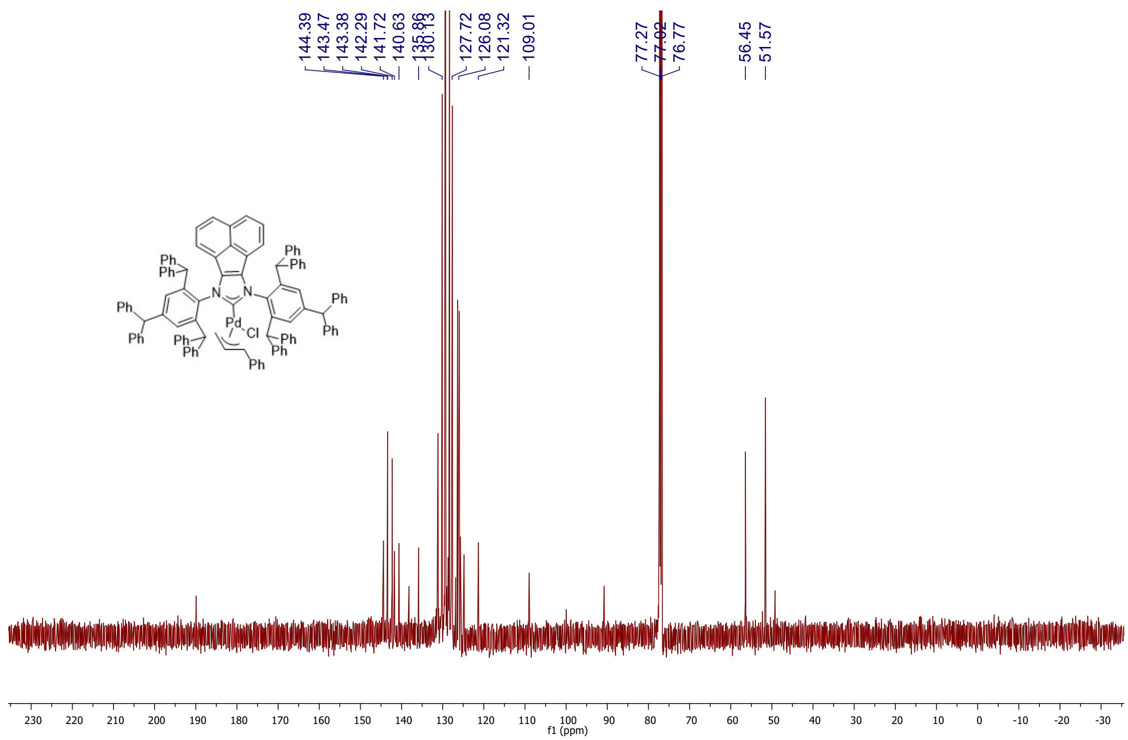
f1 (ppm)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Ph
Ph
Ph
Ph
N
N
Pd
Cl
Ph
Ph
Ph
Ph
Ph
Ph
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220
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180
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160
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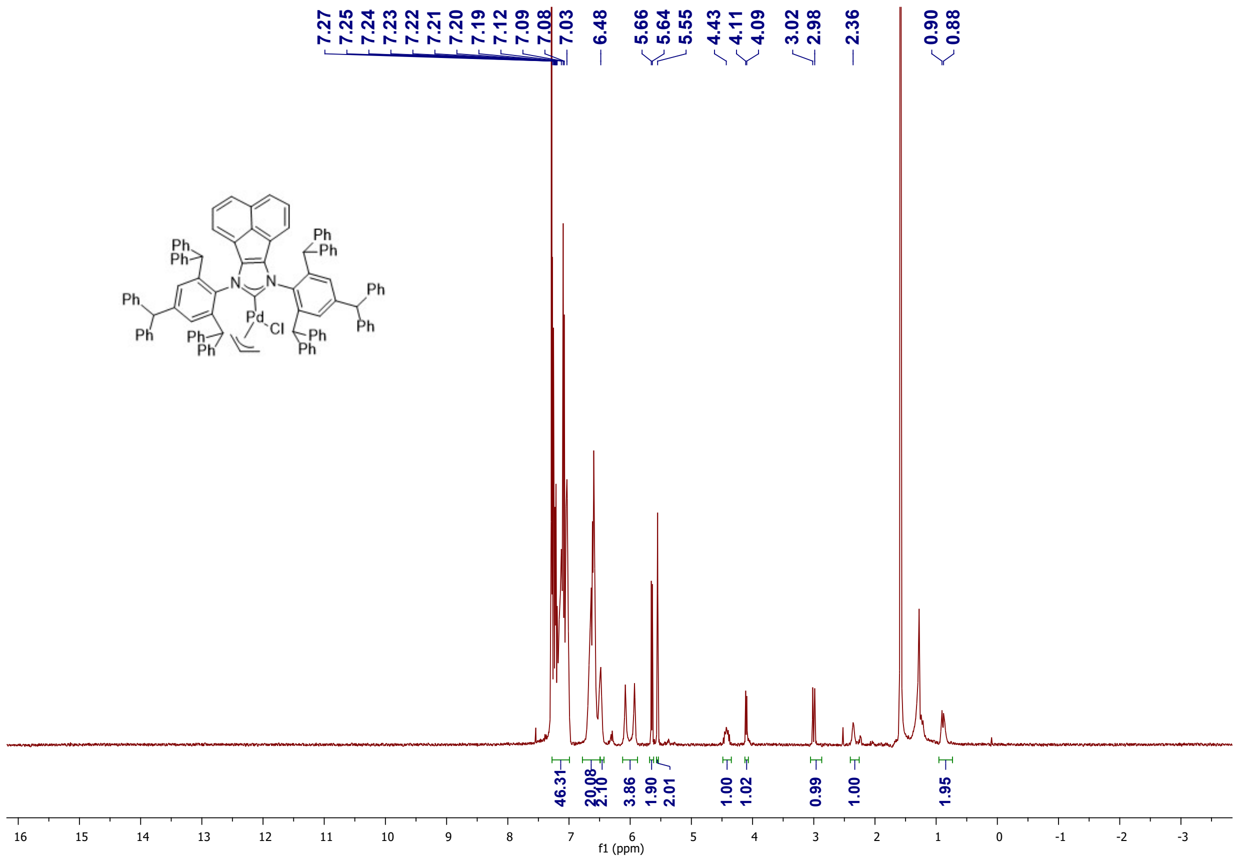
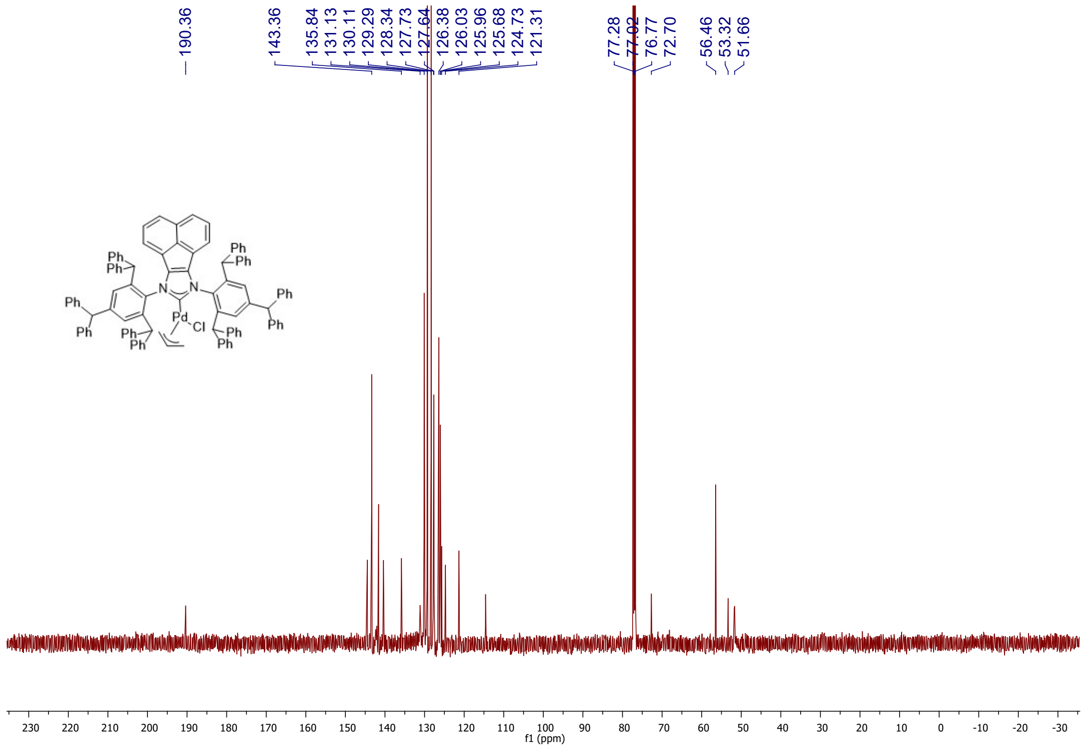
f1 (ppm)

2d

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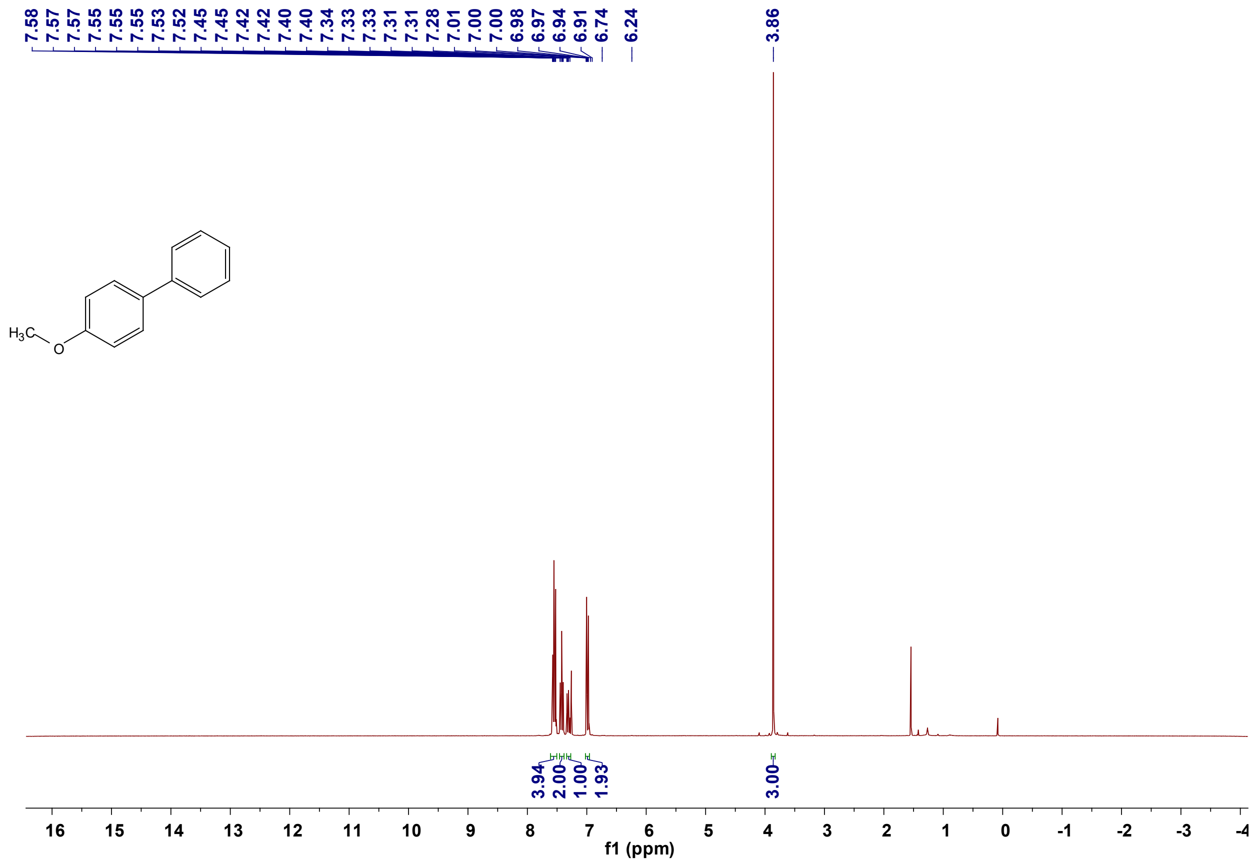
N
f1 (ppm)

3a



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6.24
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H_3C
O
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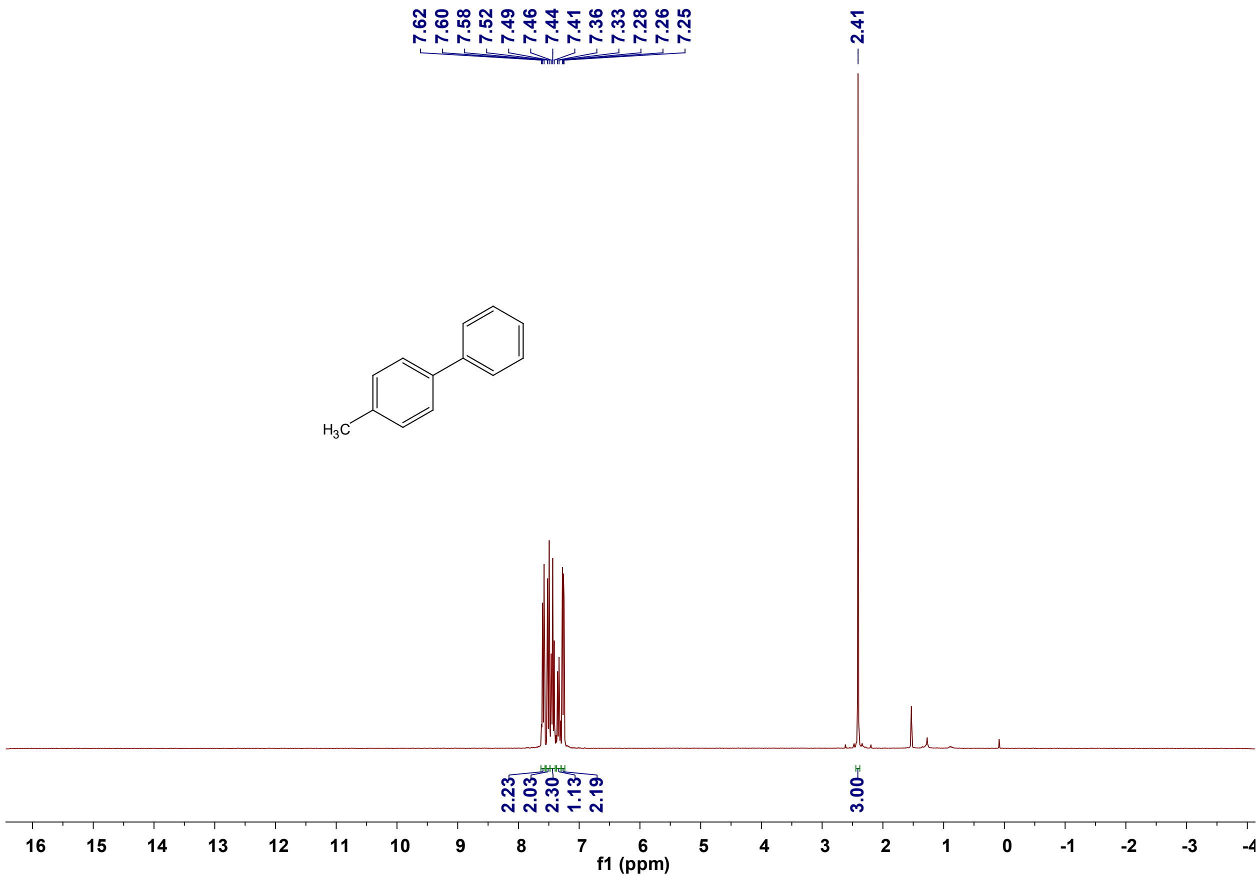
3b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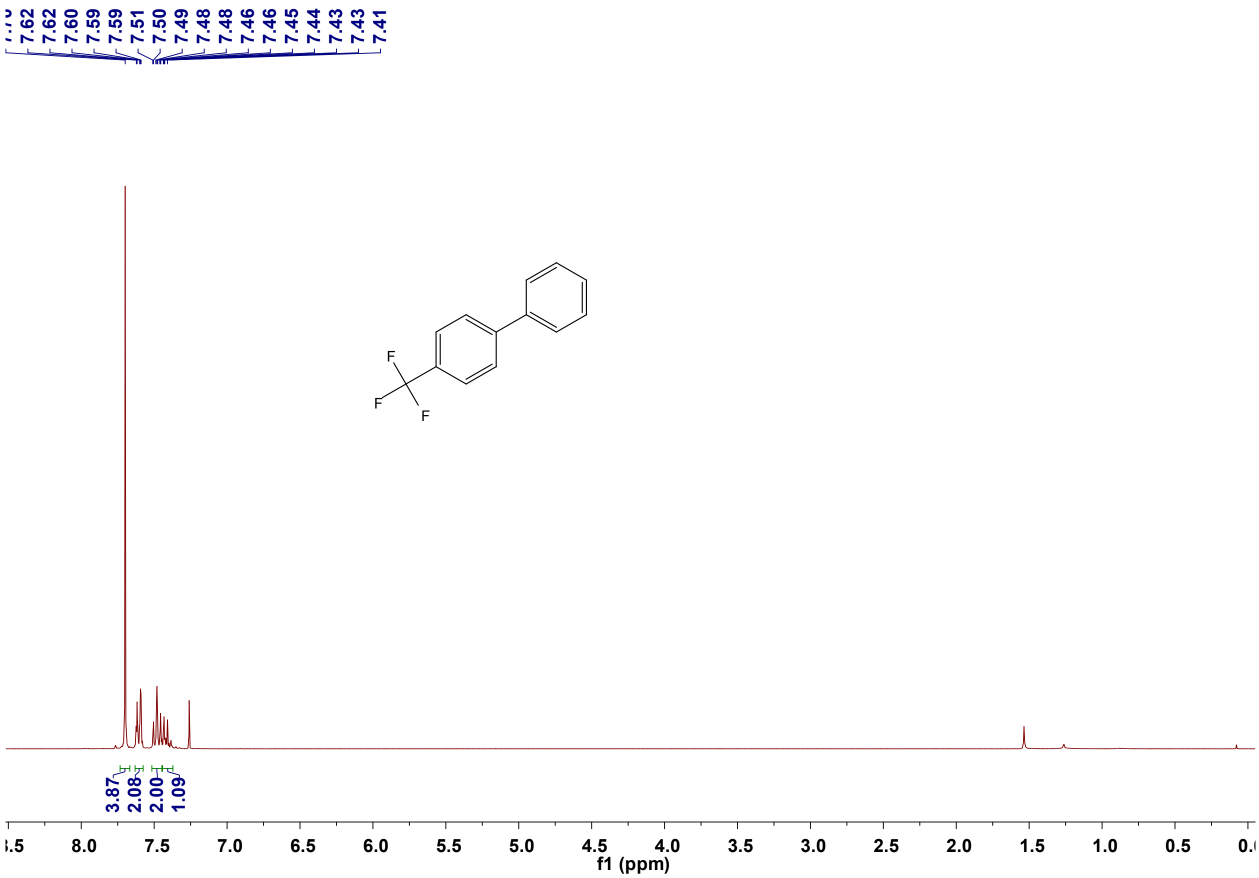
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7.43
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F
F
F
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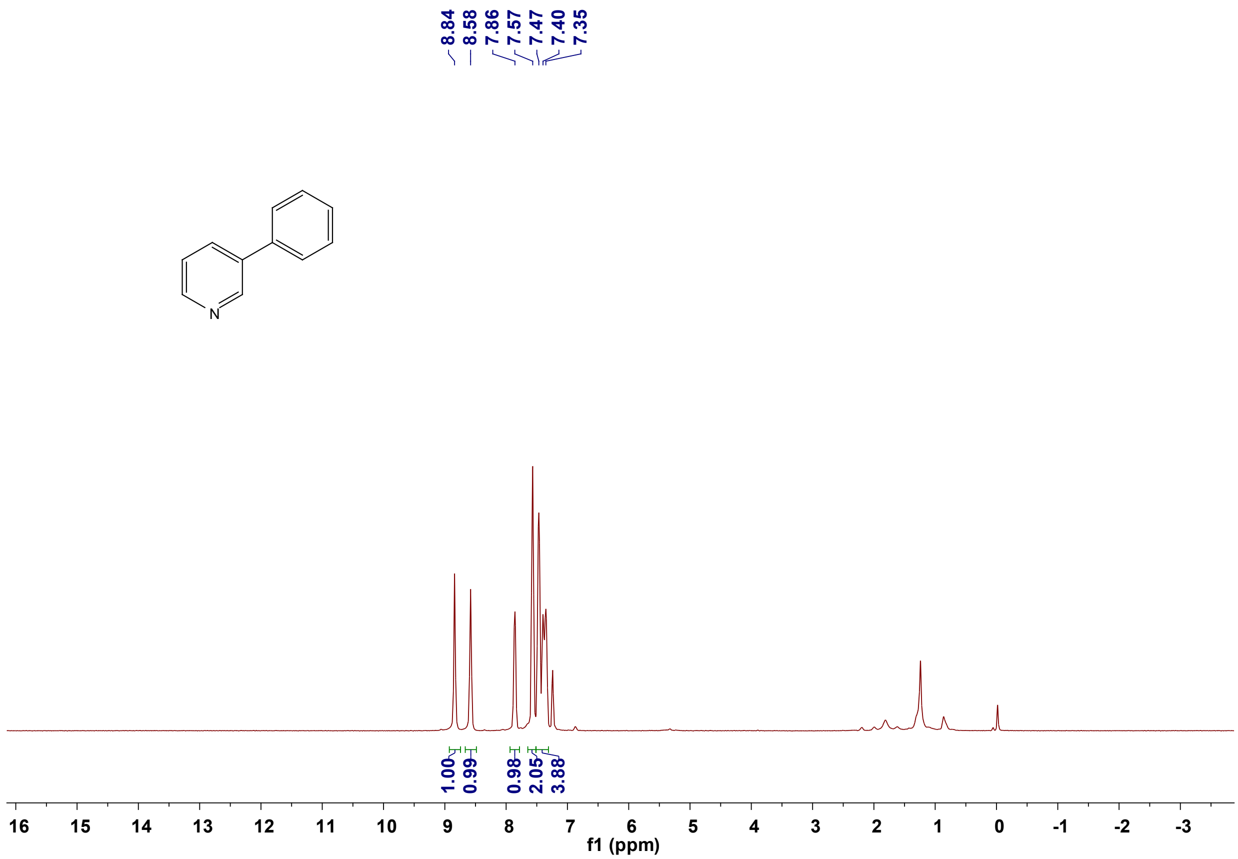

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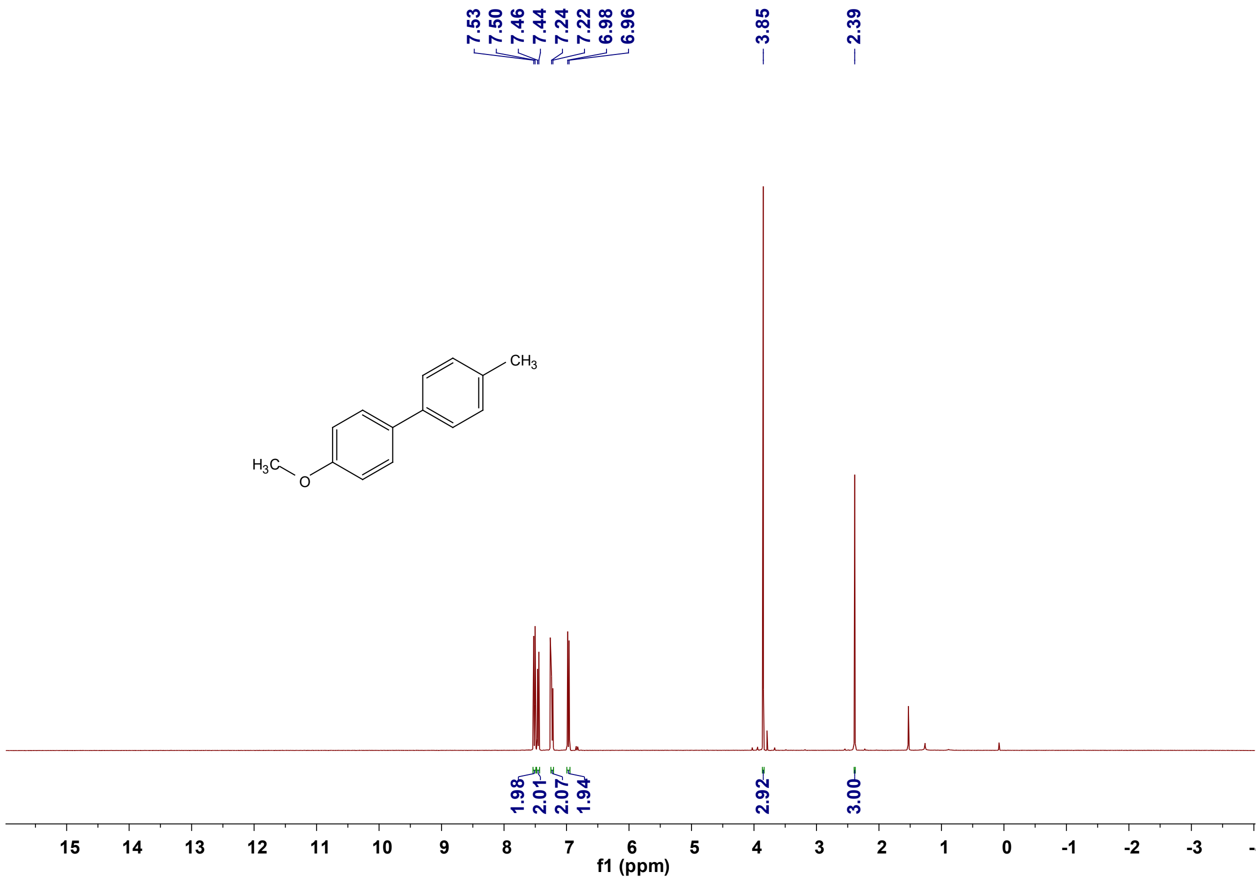
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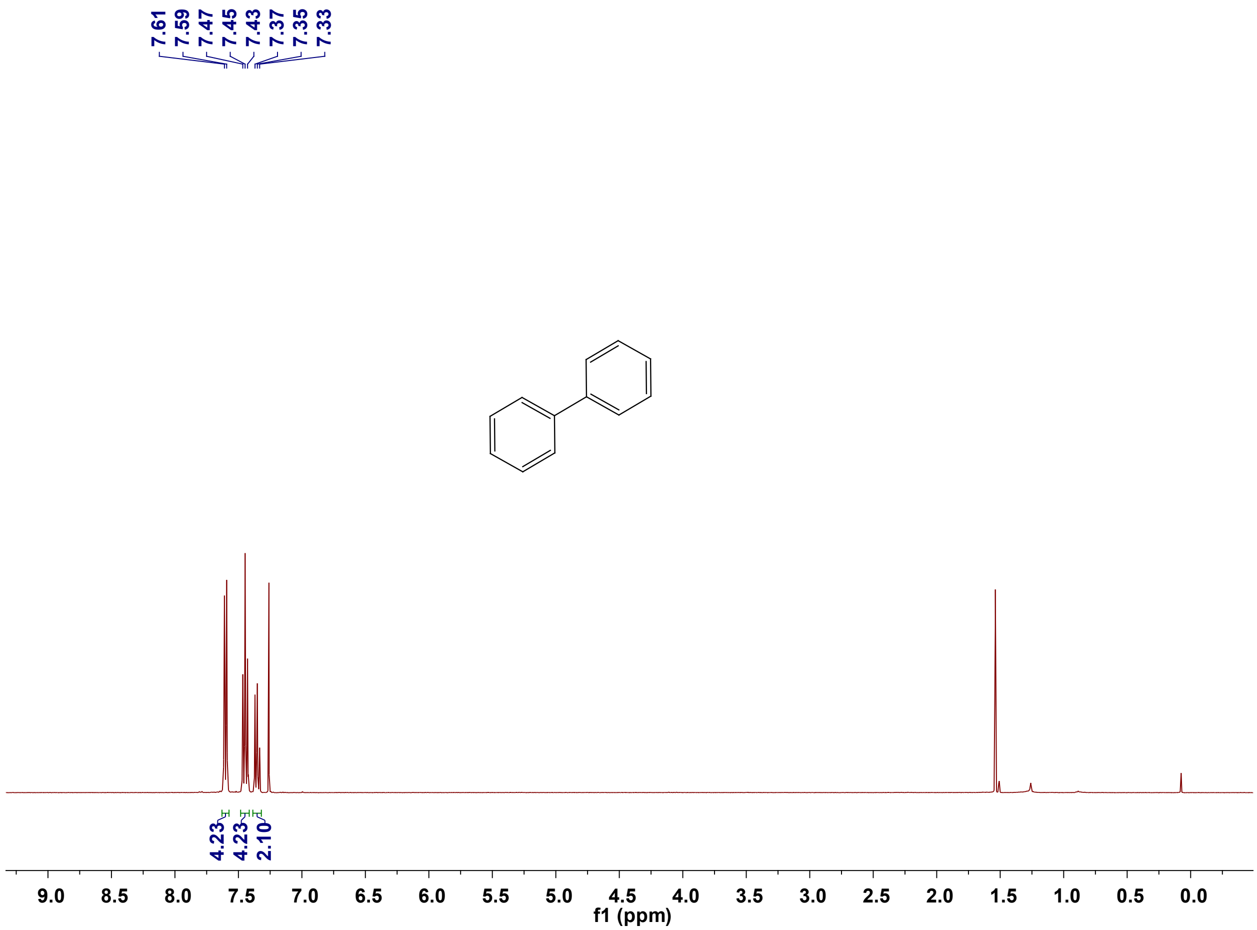
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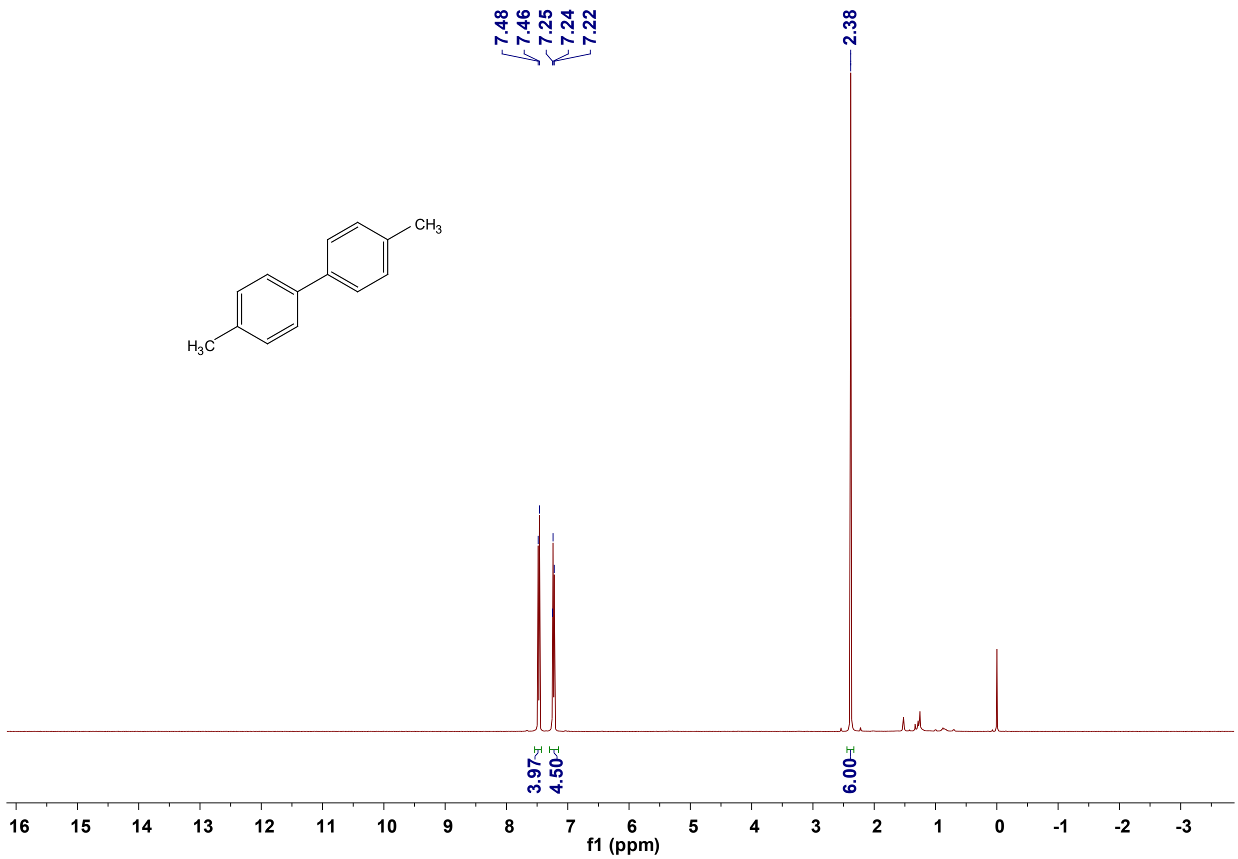
3g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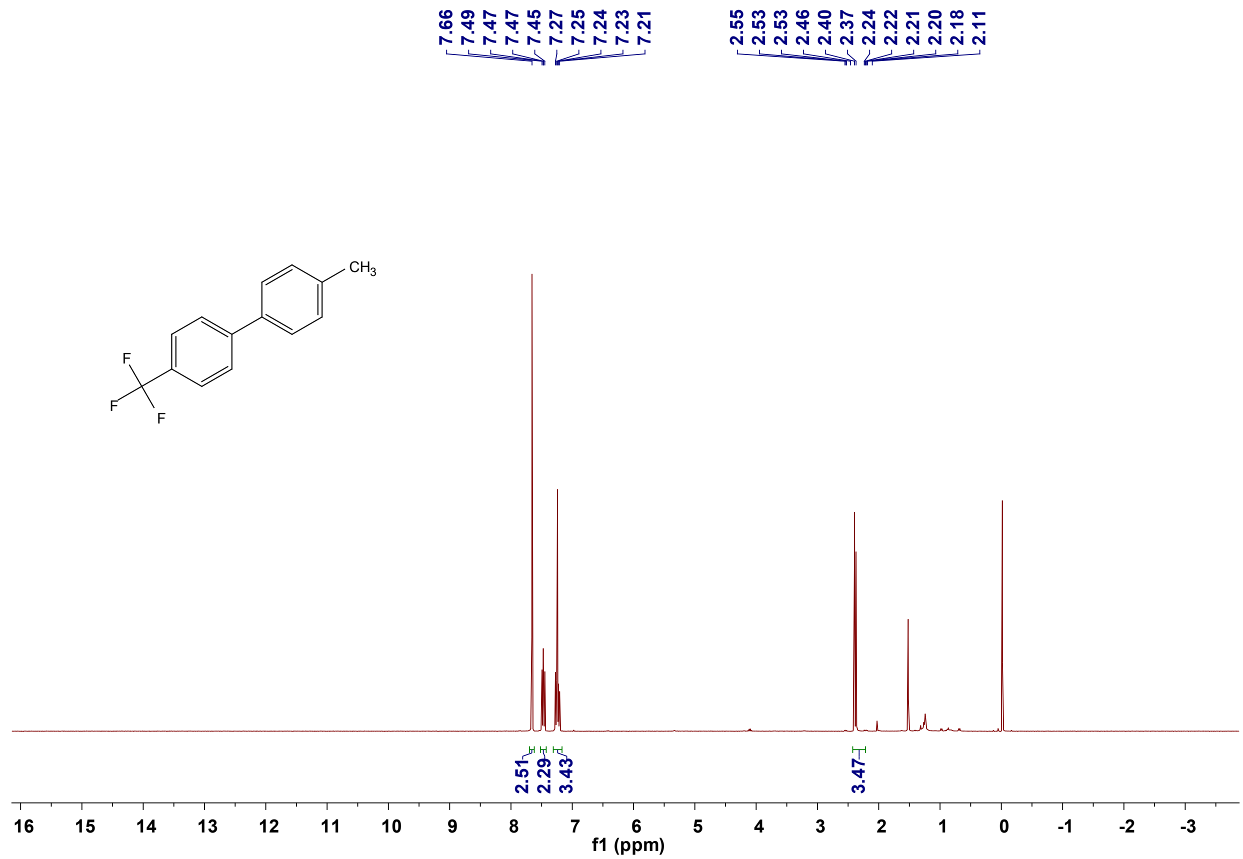
3h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2.22
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2.20
2.18
2.11
CH3
F
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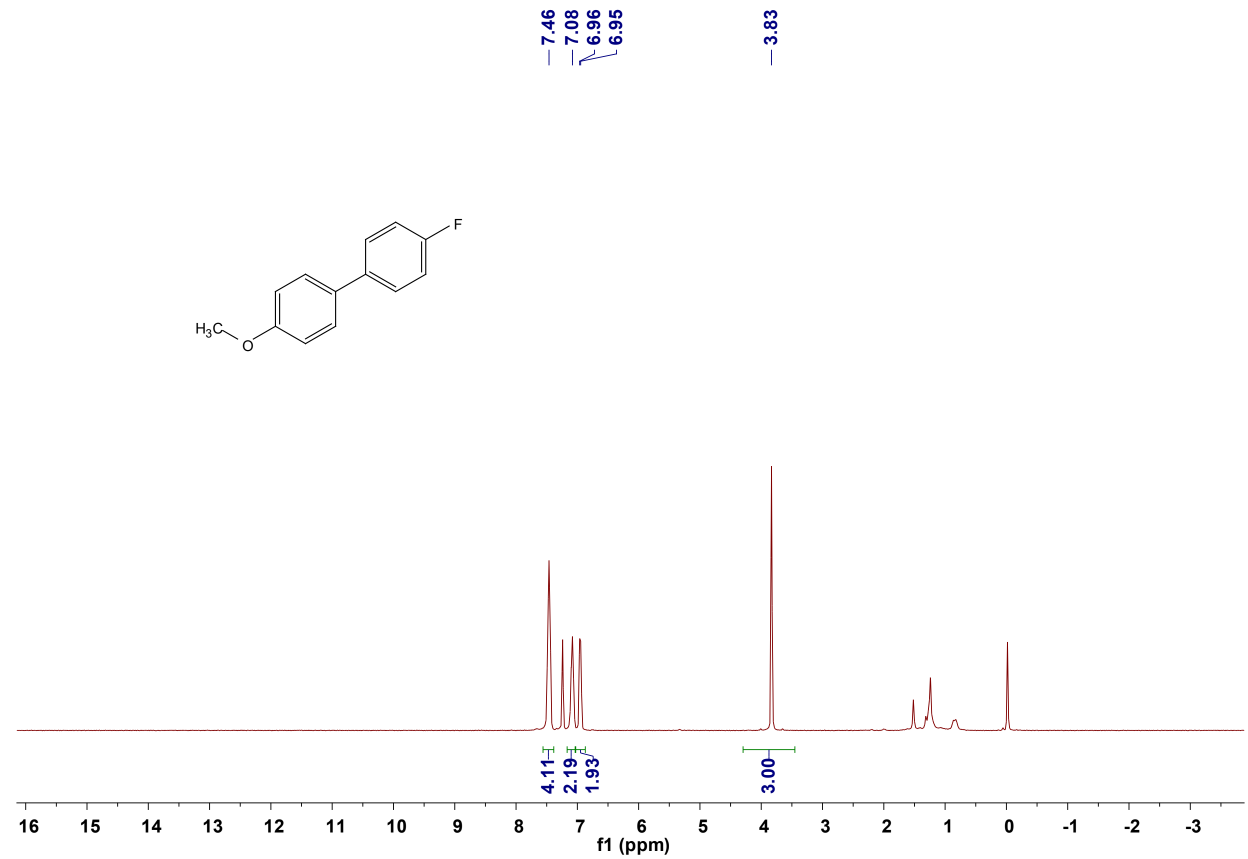
f1 (ppm)

3i



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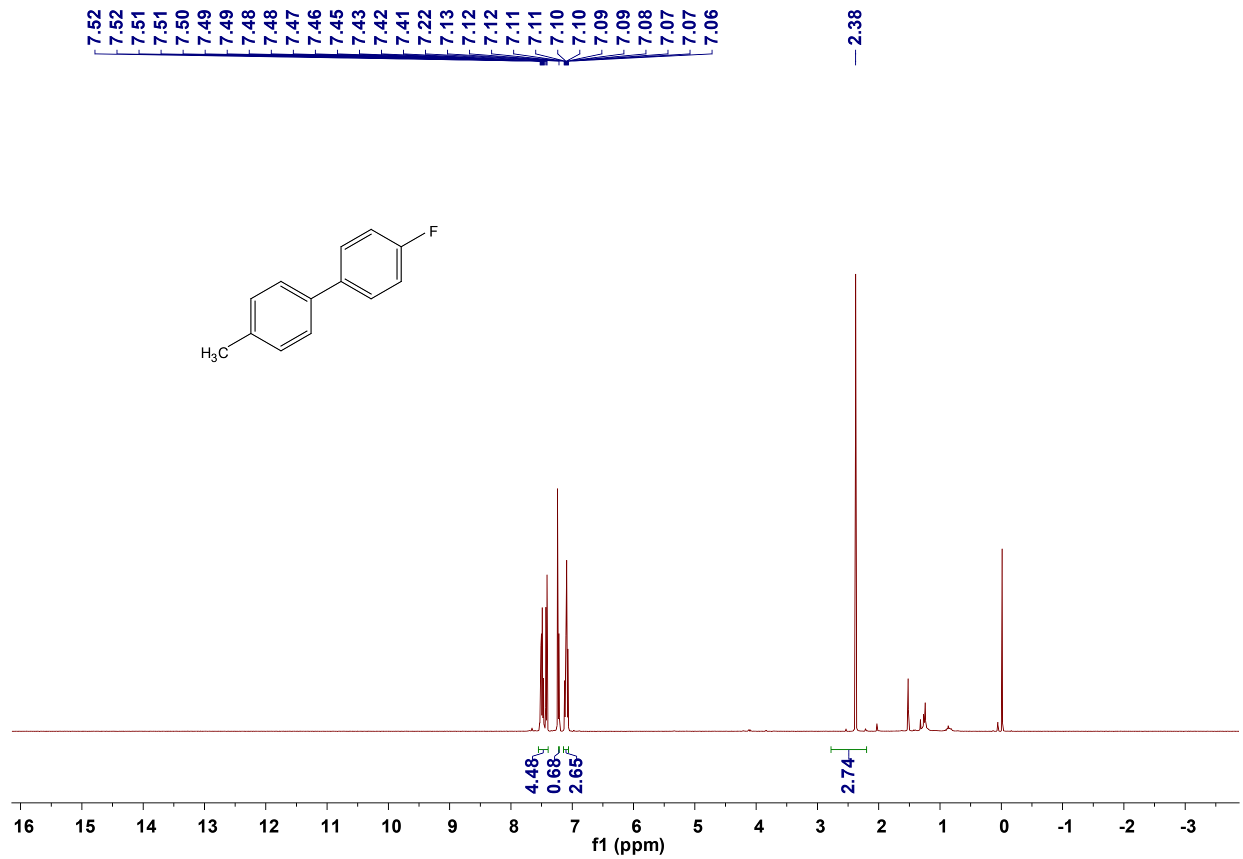
3j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F
H3C
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2.65
2.74
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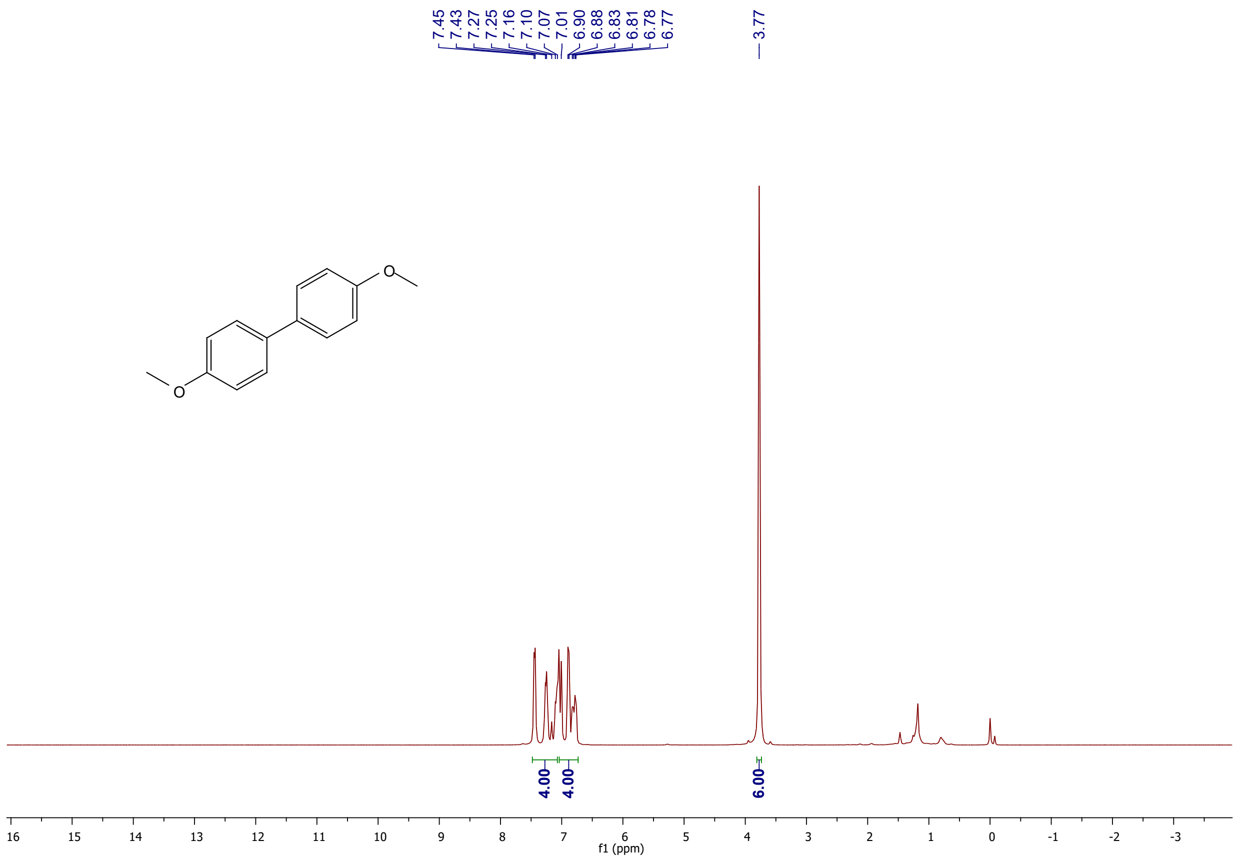
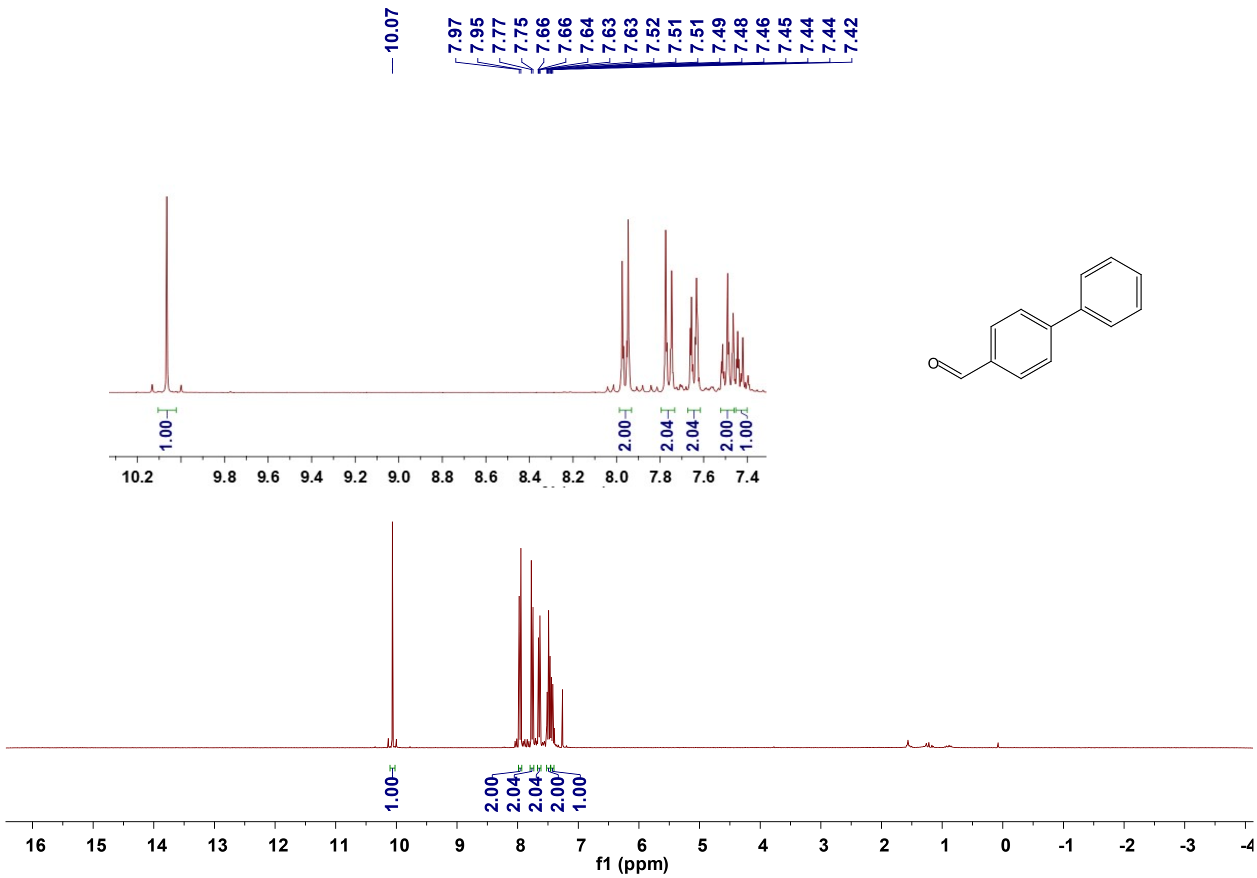
f1 (ppm)

3k

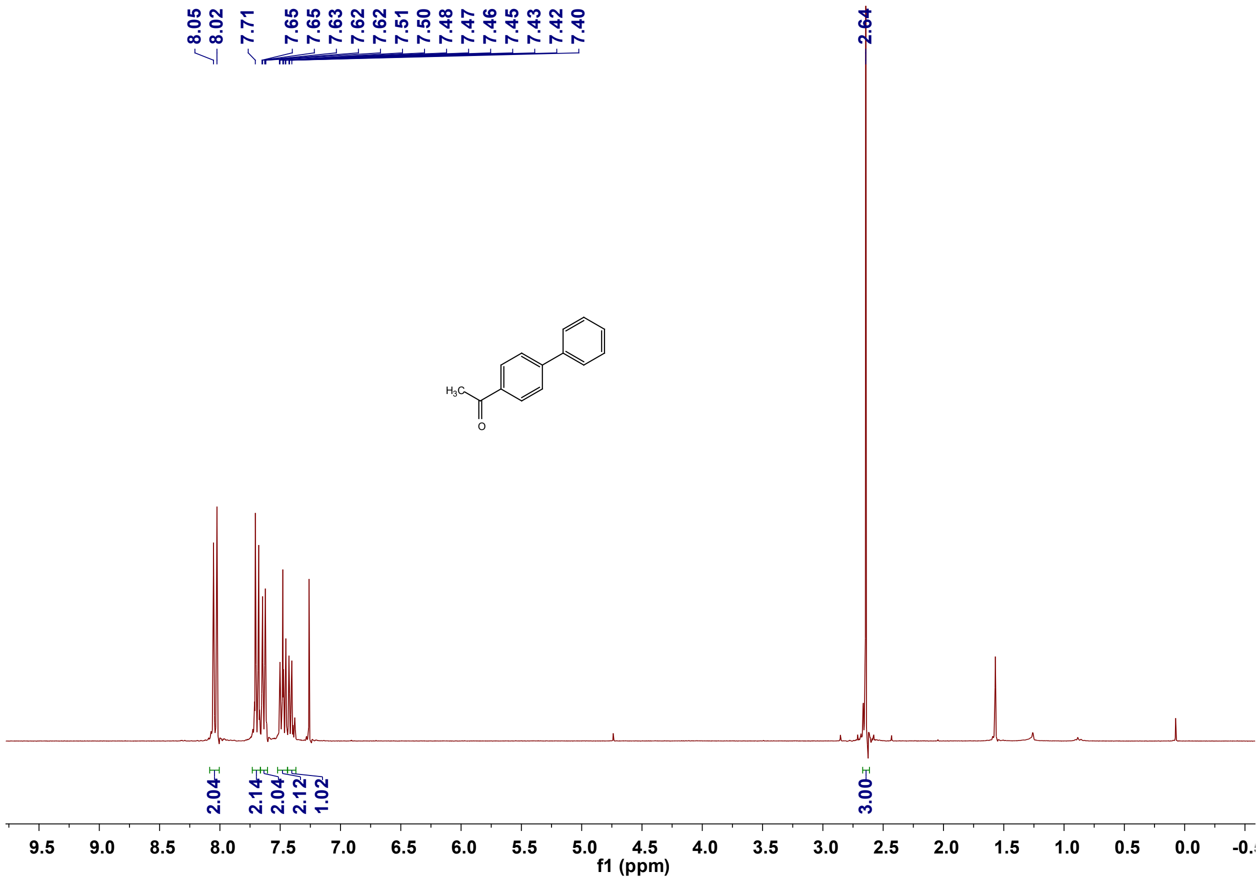


7.45
7.43
7.27
7.25
7.16
7.10
7.07
7.01
6.90
6.88
6.83
6.81
6.78
6.77
3.77
O
O
4.00
4.00
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

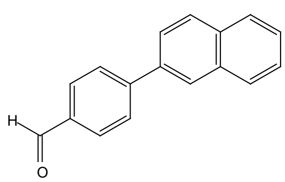
3l

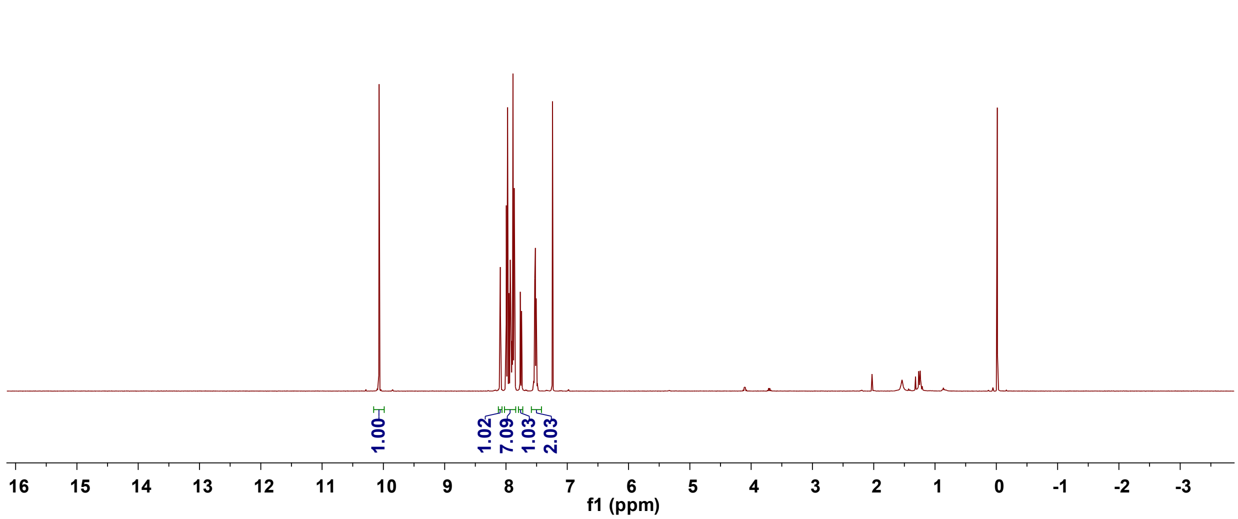


3m

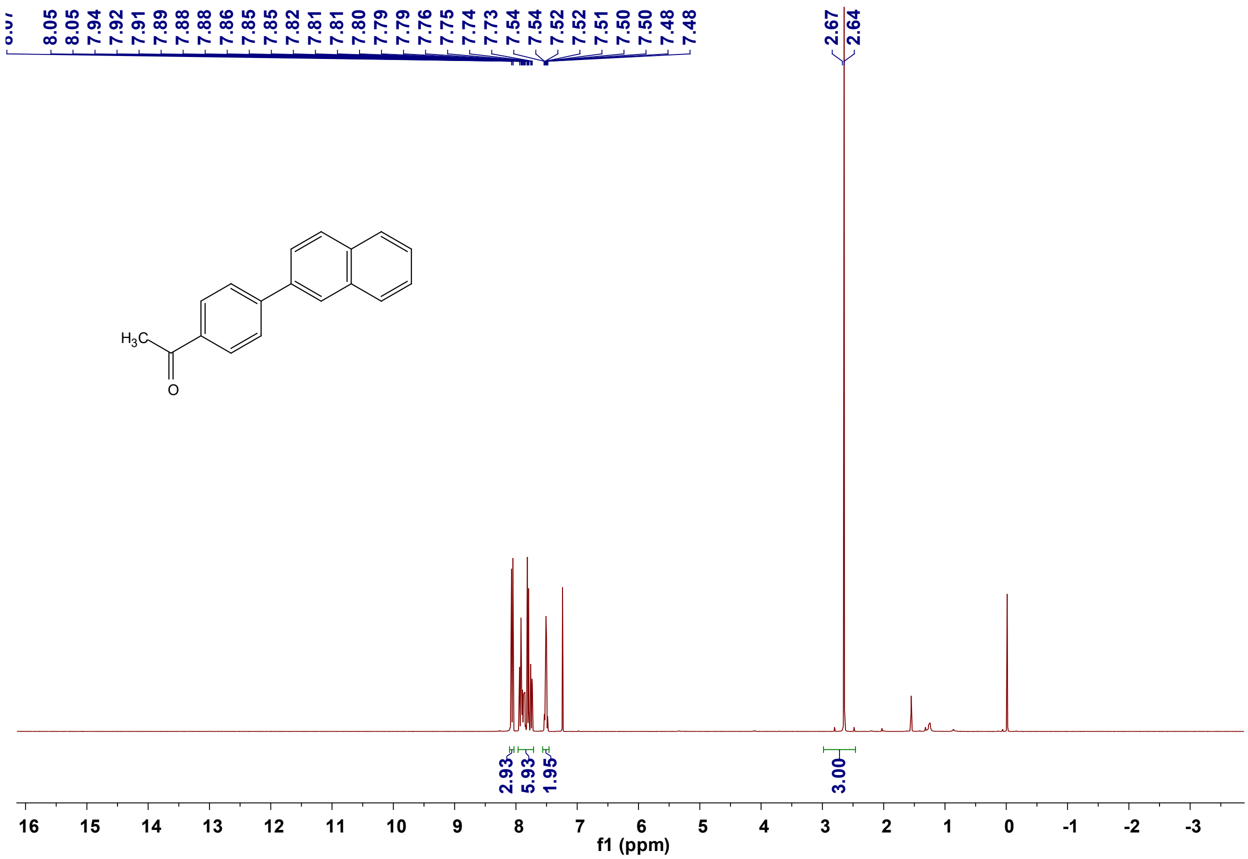

8.05
8.02
7.71
7.65
7.65
7.63
7.62
7.62
7.51
7.50
7.48
7.47
7.46
7.45
7.43
7.42
7.40
2.64
H_3C
O
2.04
2.14
2.04
2.12
1.02
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3n

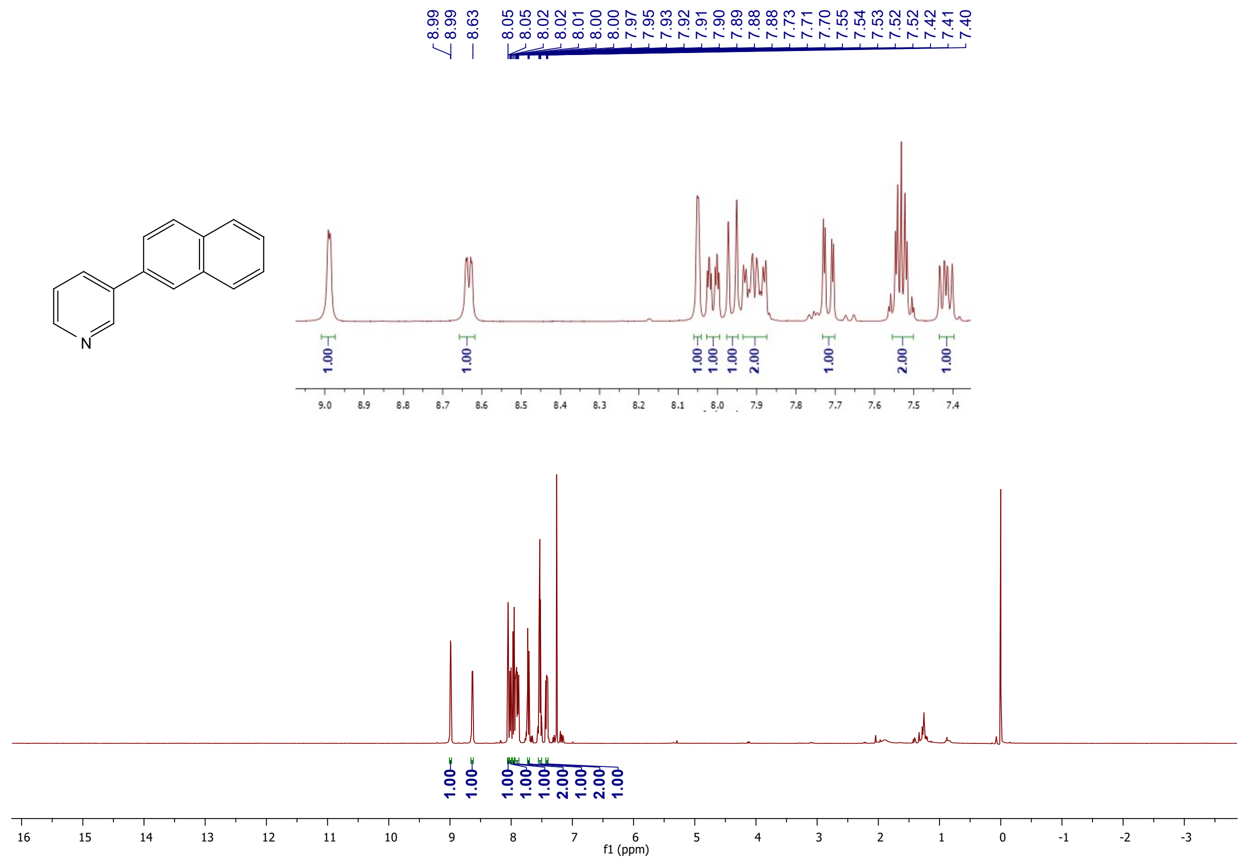



10.07
8.10
8.09
7.99
7.99
7.98
7.97
7.95
7.93
7.92
7.91
7.90
7.89
7.87
7.86
7.77
7.76
7.75
7.74
7.55
7.55
7.53
7.53
7.52
7.51
7.51
7.51
7.50
7.49
1.00
1.02
7.09
1.03
2.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

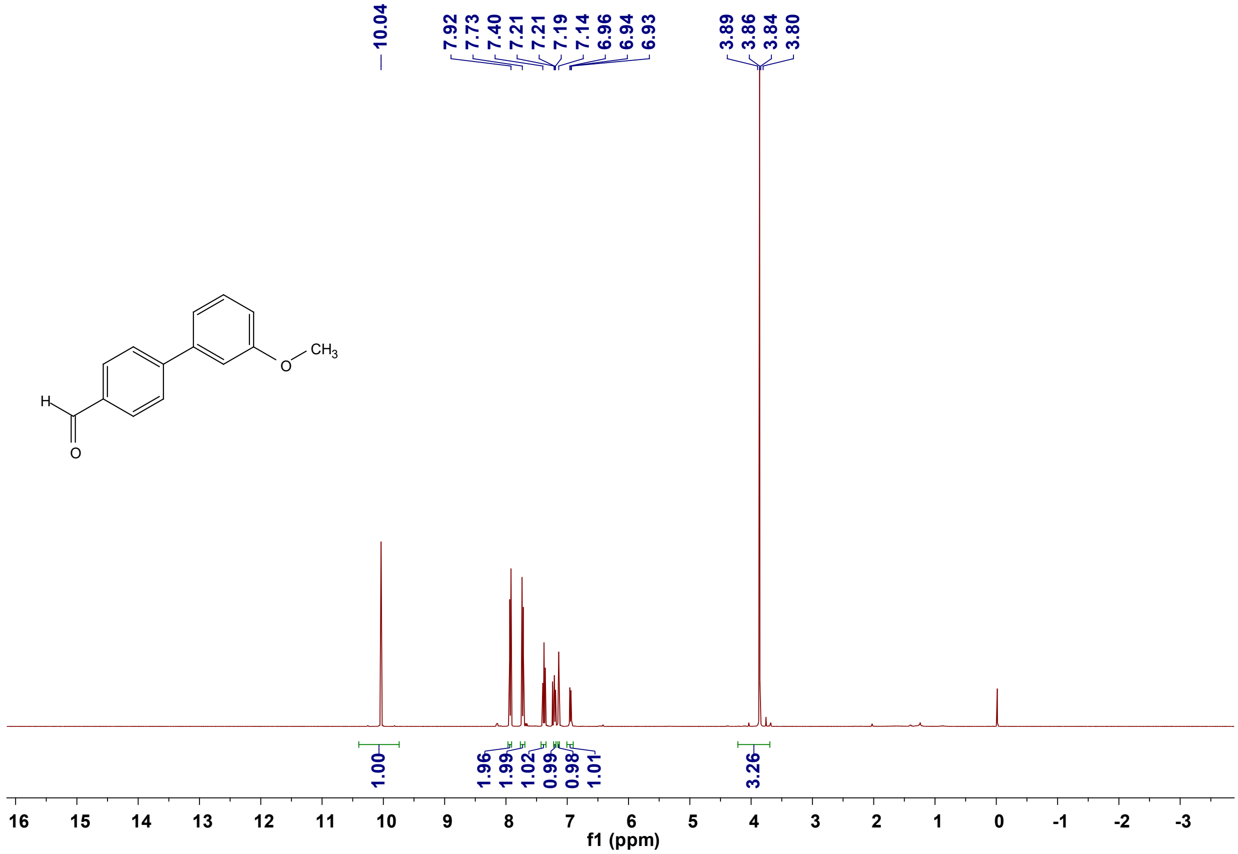
3o



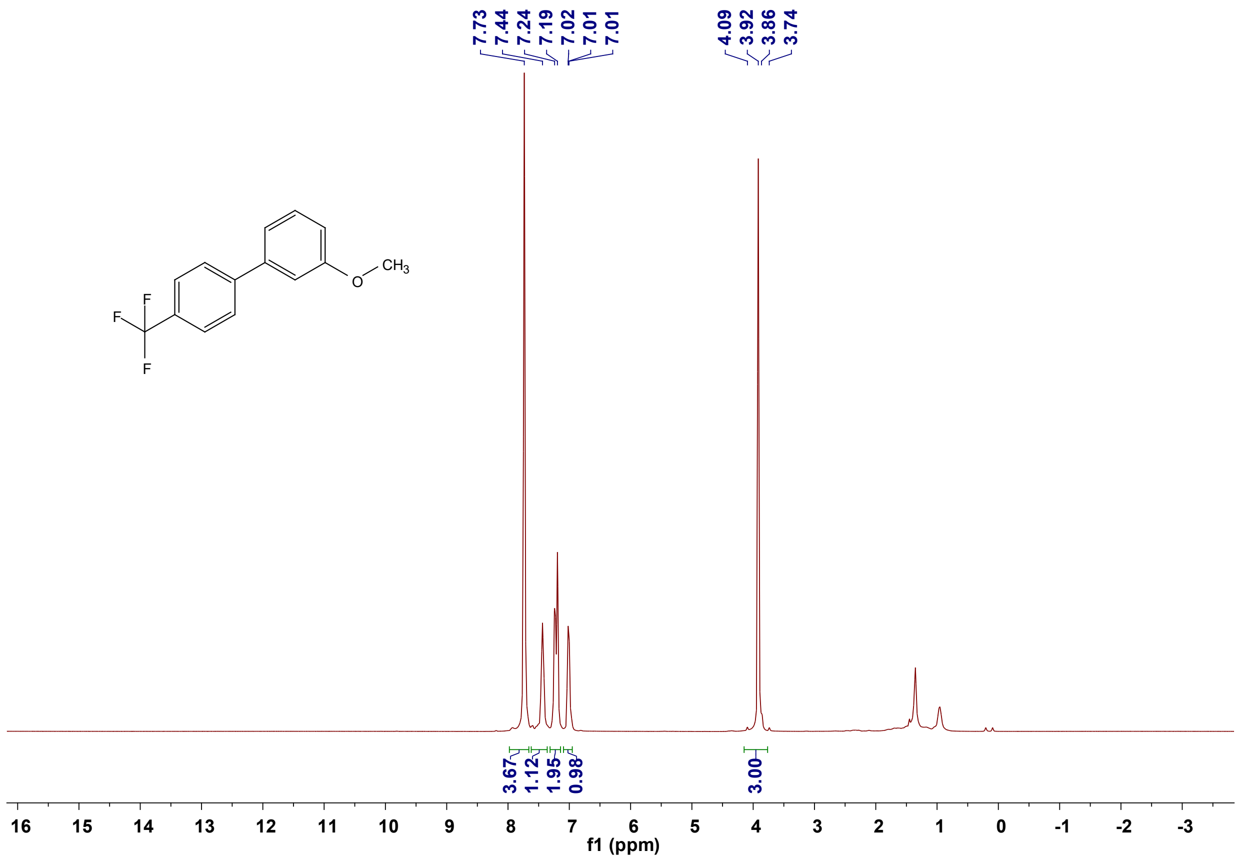
3p


8.99
8.99
8.63
8.05
8.05
8.02
8.02
8.01
8.00
8.00
7.97
7.95
7.93
7.92
7.91
7.90
7.89
7.88
7.88
7.73
7.71
7.70
7.55
7.54
7.53
7.52
7.52
7.42
7.41
7.40
N
f1 (ppm)

3q

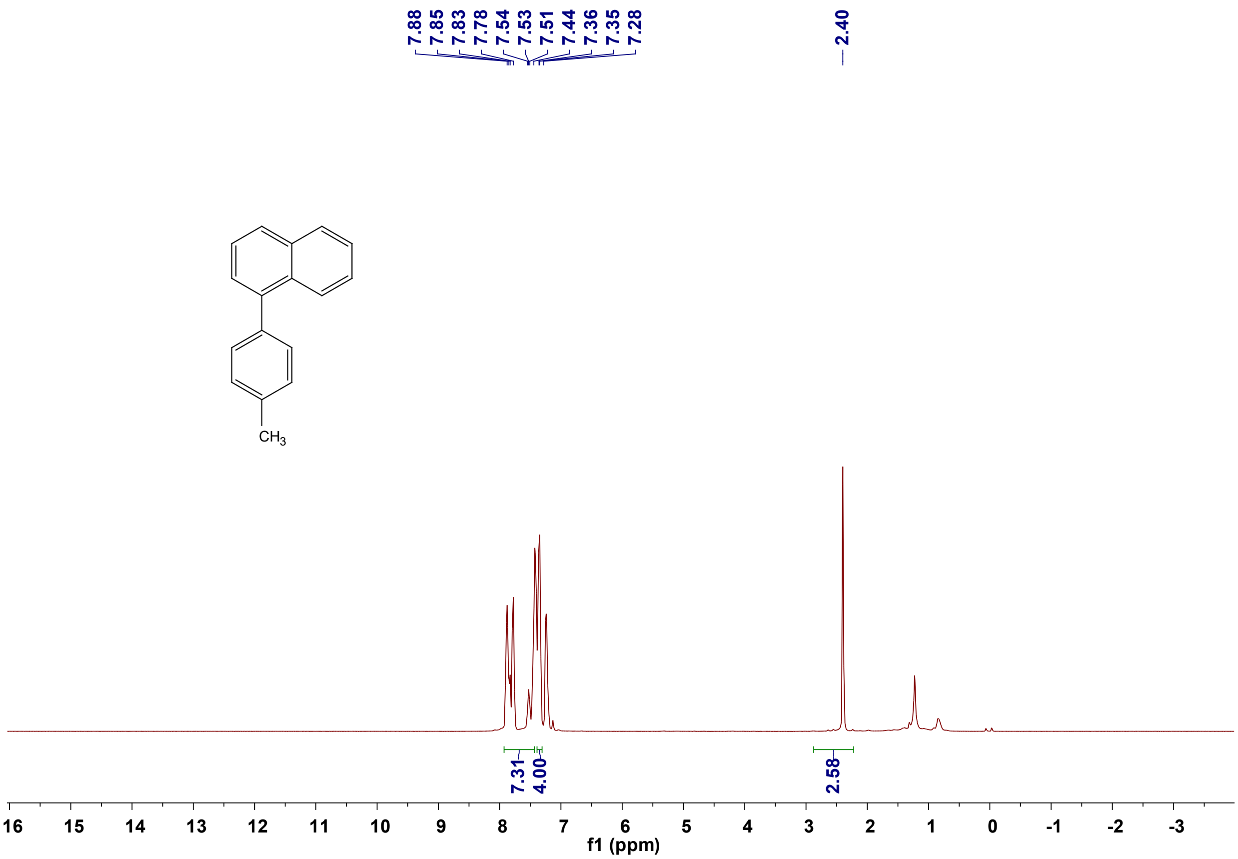

10.04
7.92
7.73
7.40
7.21
7.21
7.19
7.14
6.96
6.94
6.93
3.89
3.86
3.84
3.80
1.00
1.96
1.99
1.02
0.99
0.98
1.01
3.26
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

3r



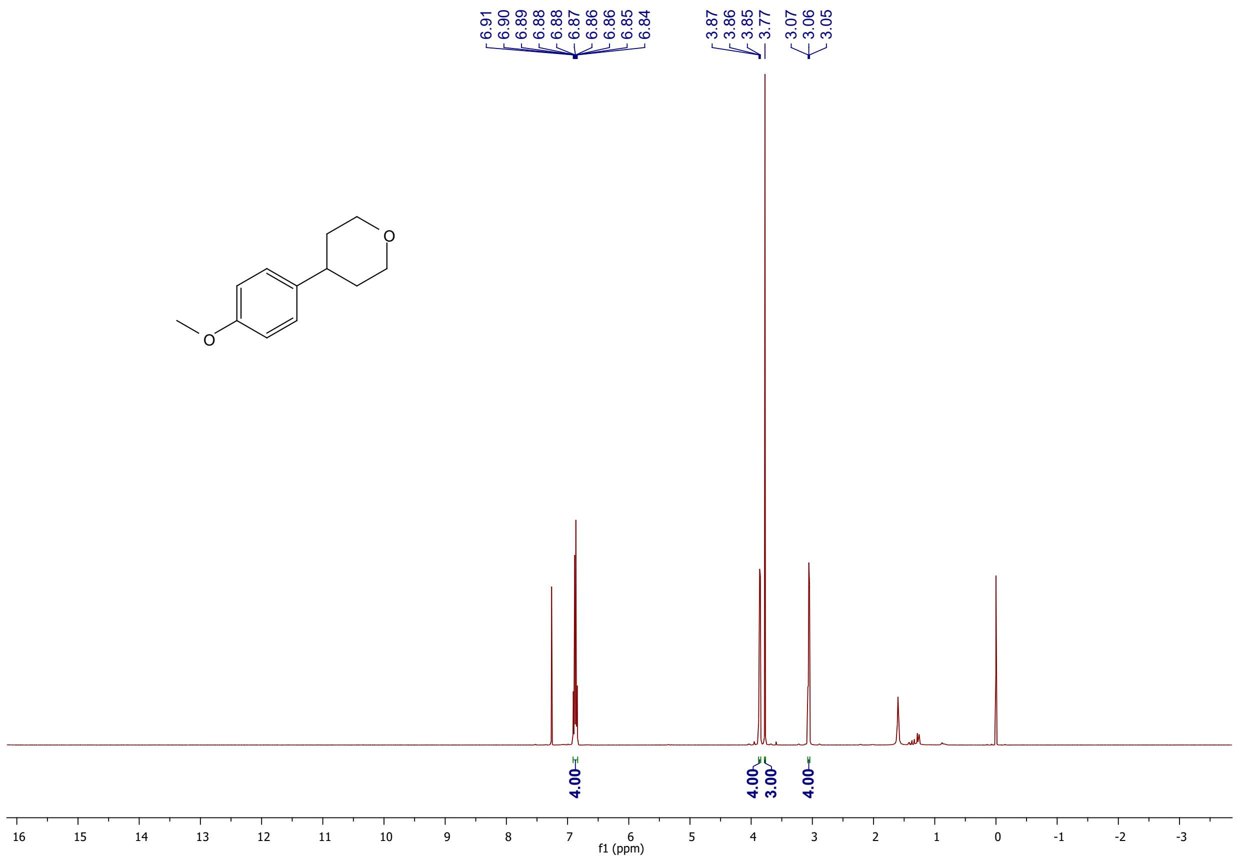
7.73
7.44
7.24
7.19
7.02
7.01
7.01
4.09
3.92
3.86
3.74
CH3
O
F
F
F
3.67
1.12
1.95
0.98
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

3s



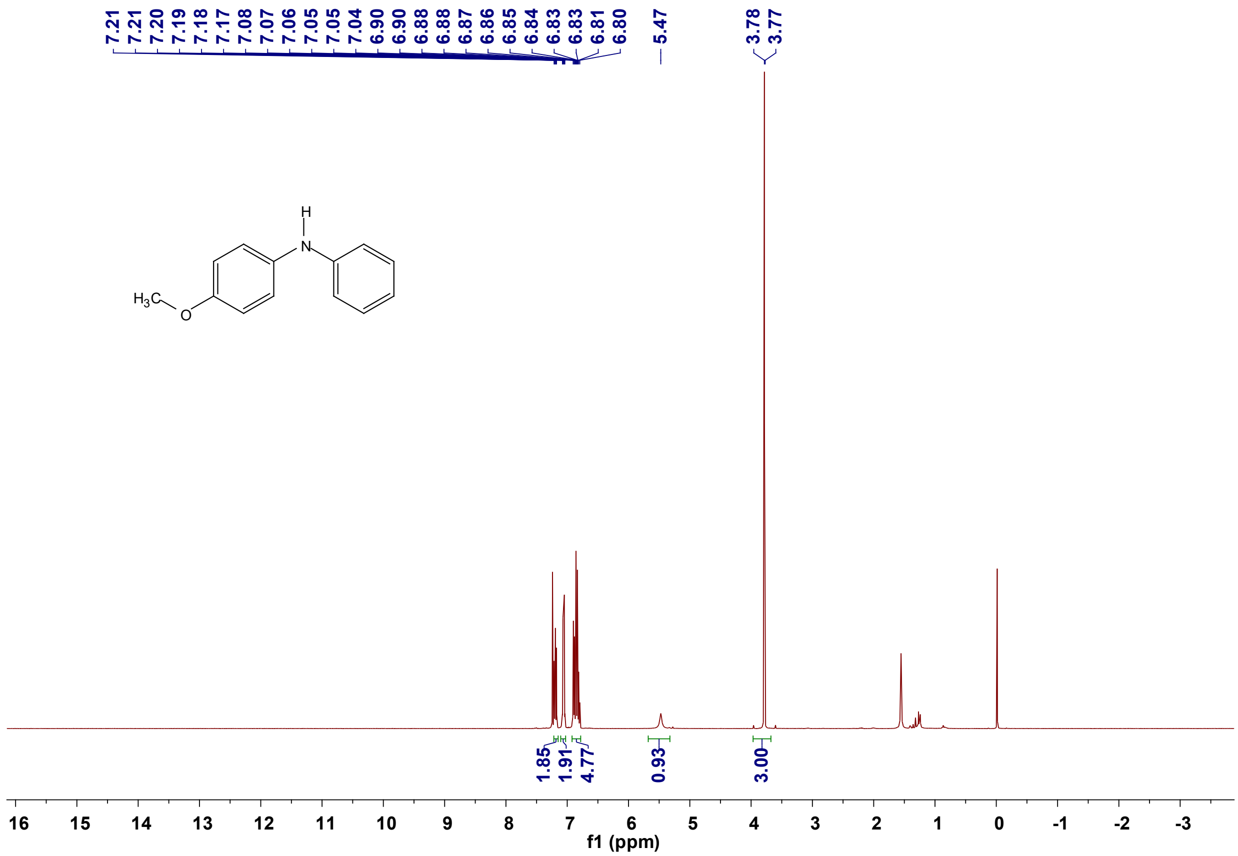
7.88
7.85
7.83
7.78
7.54
7.53
7.51
7.44
7.36
7.35
7.28
2.40
CH3
7.31
4.00
2.58
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4a

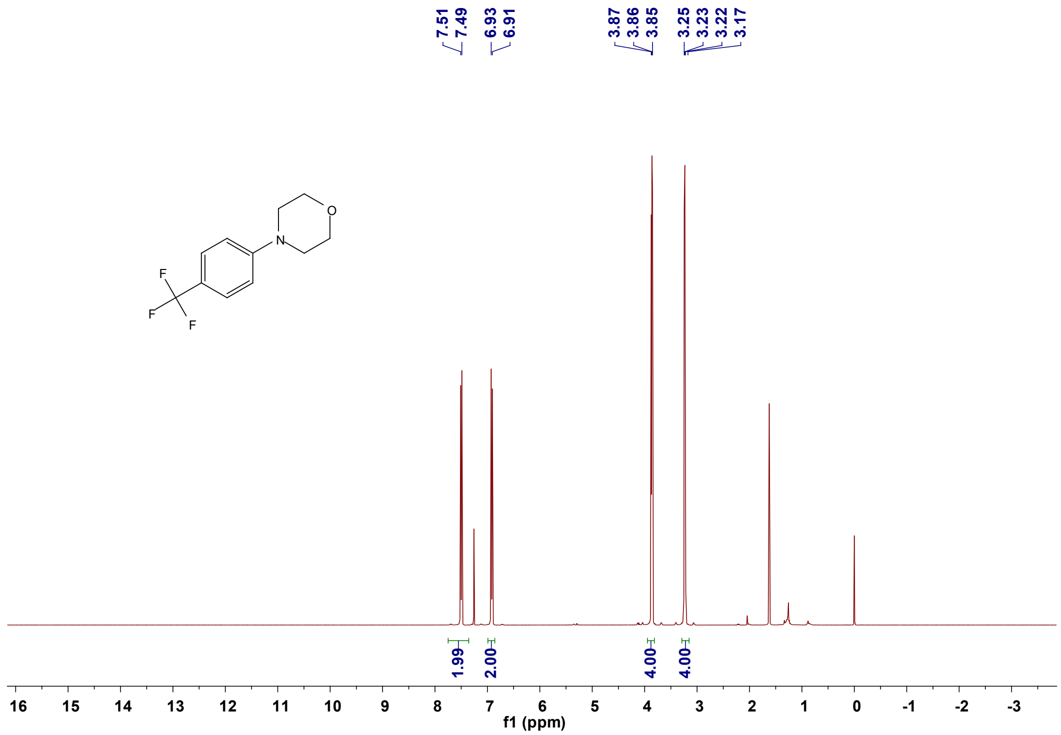


6.91
6.90
6.89
6.88
6.88
6.87
6.86
6.86
6.85
6.84
3.87
3.86
3.85
3.77
3.07
3.06
3.05
4.00
4.00
3.00
4.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

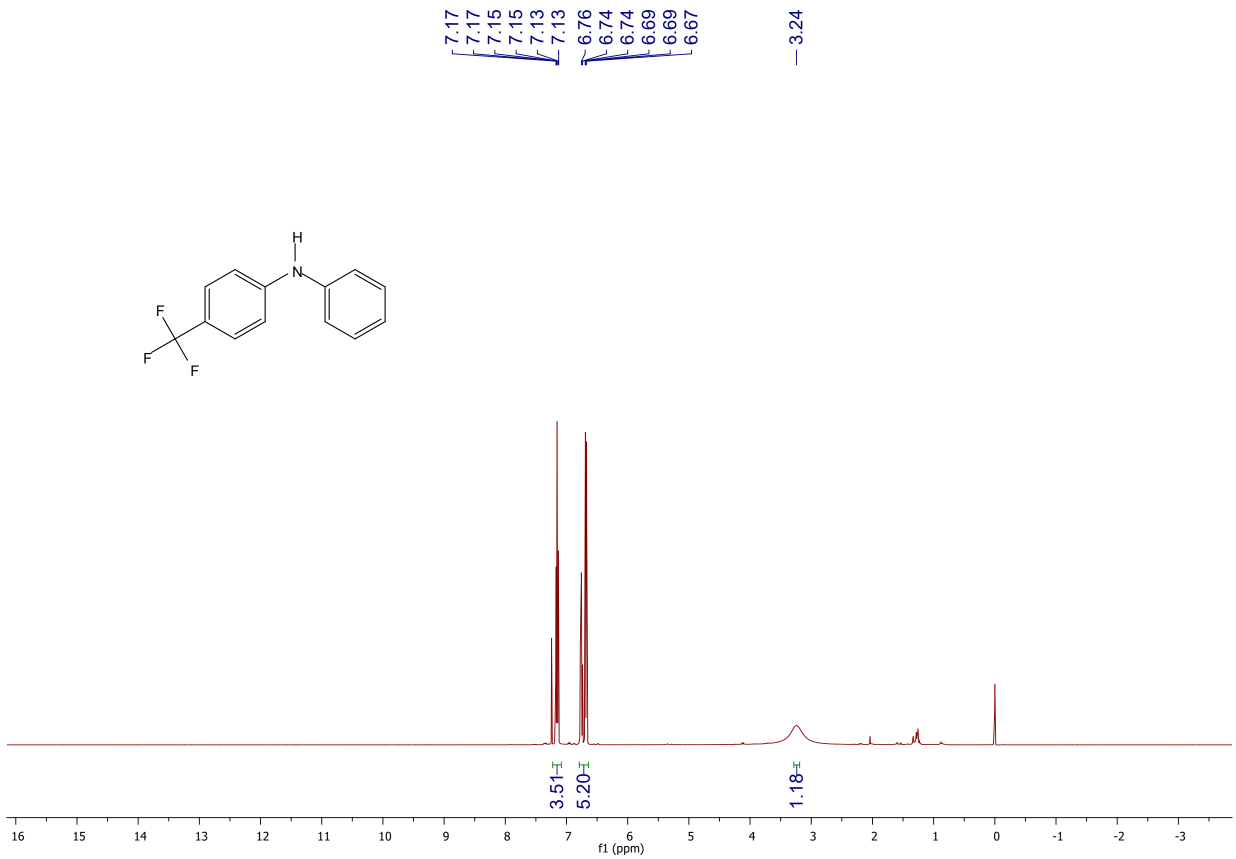
4b


7.21
7.21
7.20
7.19
7.18
7.17
7.08
7.07
7.06
7.05
7.05
7.04
6.90
6.90
6.88
6.88
6.87
6.86
6.85
6.84
6.83
6.83
6.81
6.80
5.47
3.78
3.77
H
N
H_3C
O
1.85
1.91
4.77
0.93
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

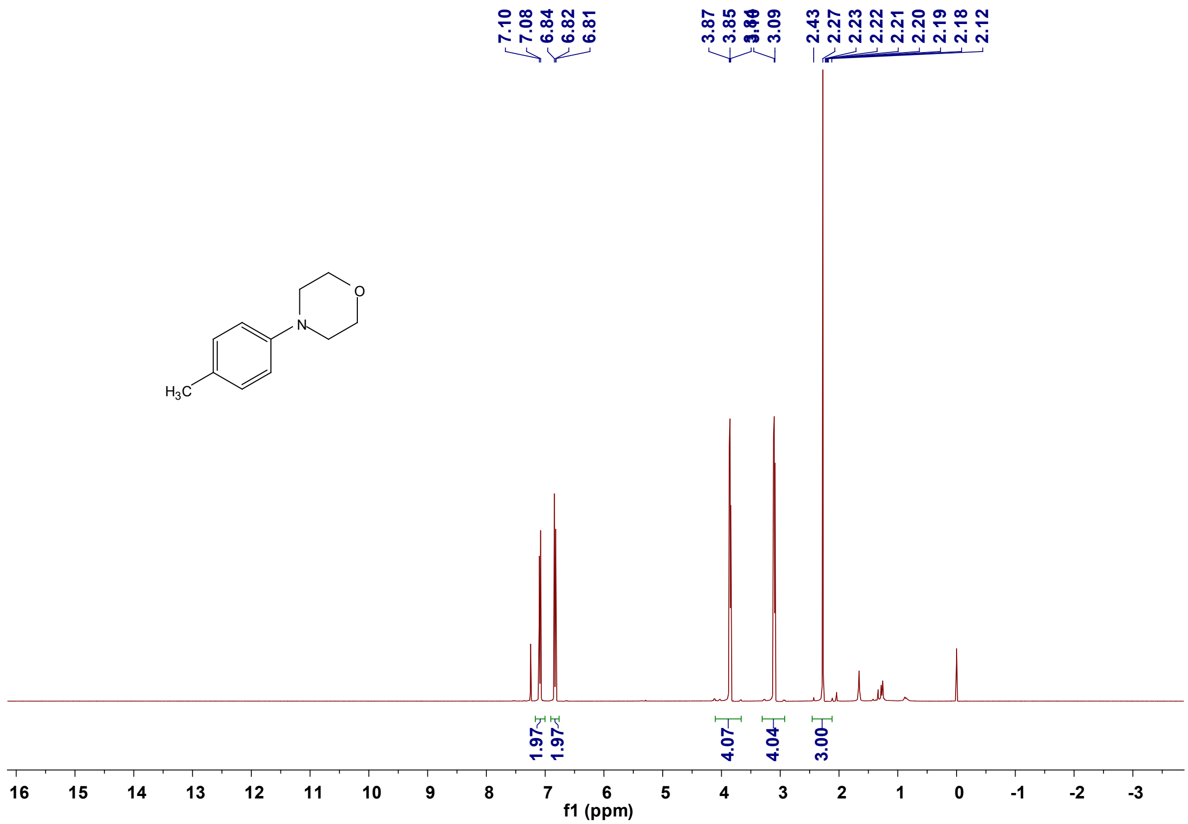
4c


7.51
7.49
6.93
6.91
3.87
3.86
3.85
3.25
3.23
3.22
3.17
F
F
F
N
O
1.99
2.00
4.00
4.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

4d

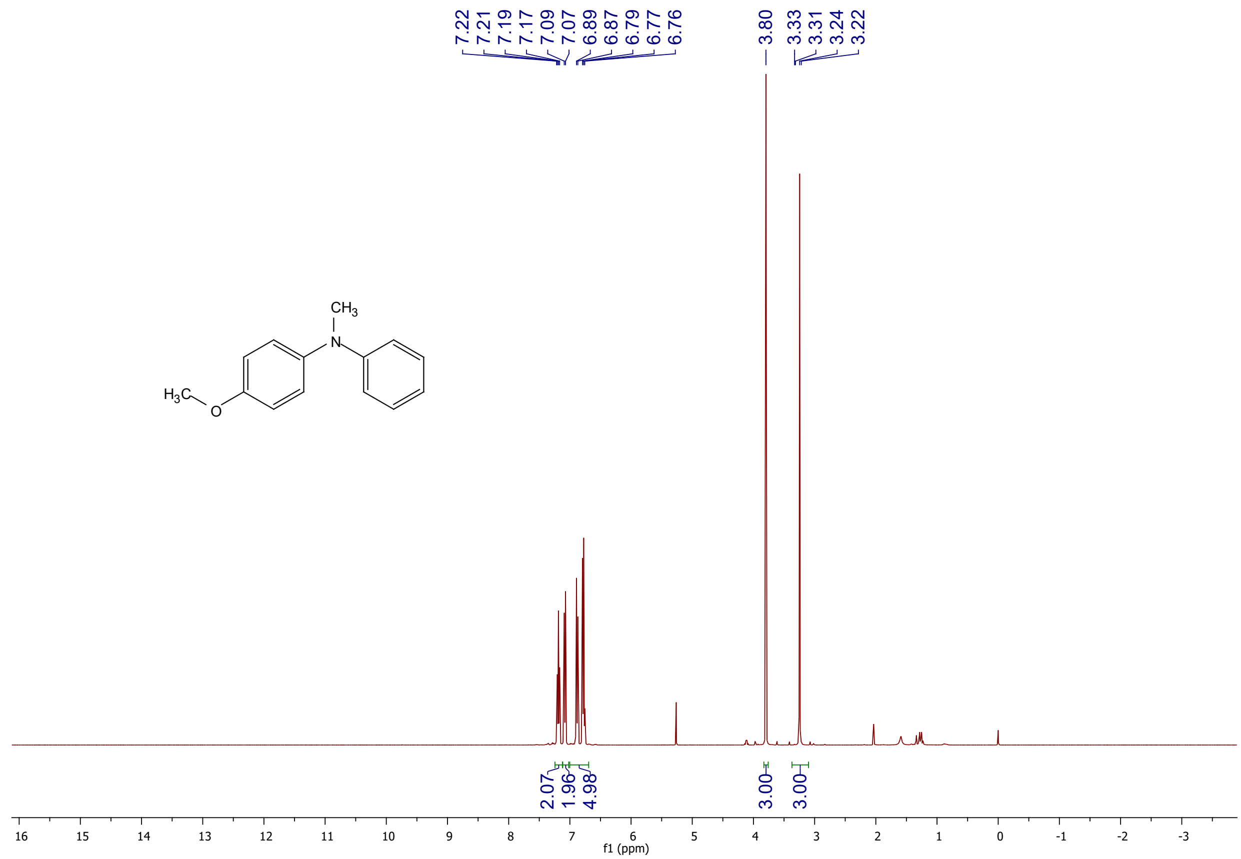

7.17
7.17
7.15
7.15
7.13
7.13
6.76
6.74
6.74
6.69
6.69
6.67
3.24
3.51
5.20
1.18
f1 (ppm)

4e

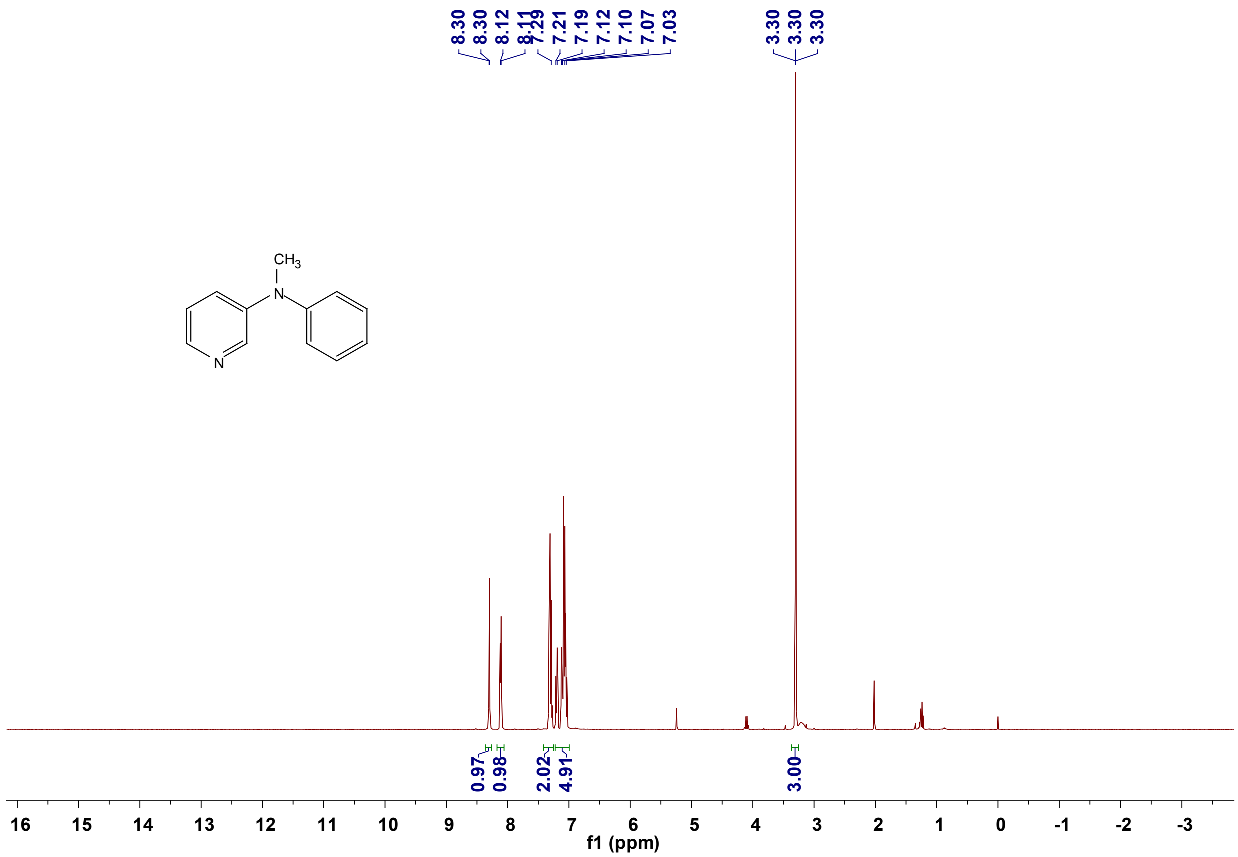


7.10
7.08
6.84
6.82
6.81
3.87
3.85
3.09
2.43
2.27
2.23
2.22
2.21
2.20
2.19
2.18
2.12
1.97
1.97
4.07
4.04
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4f

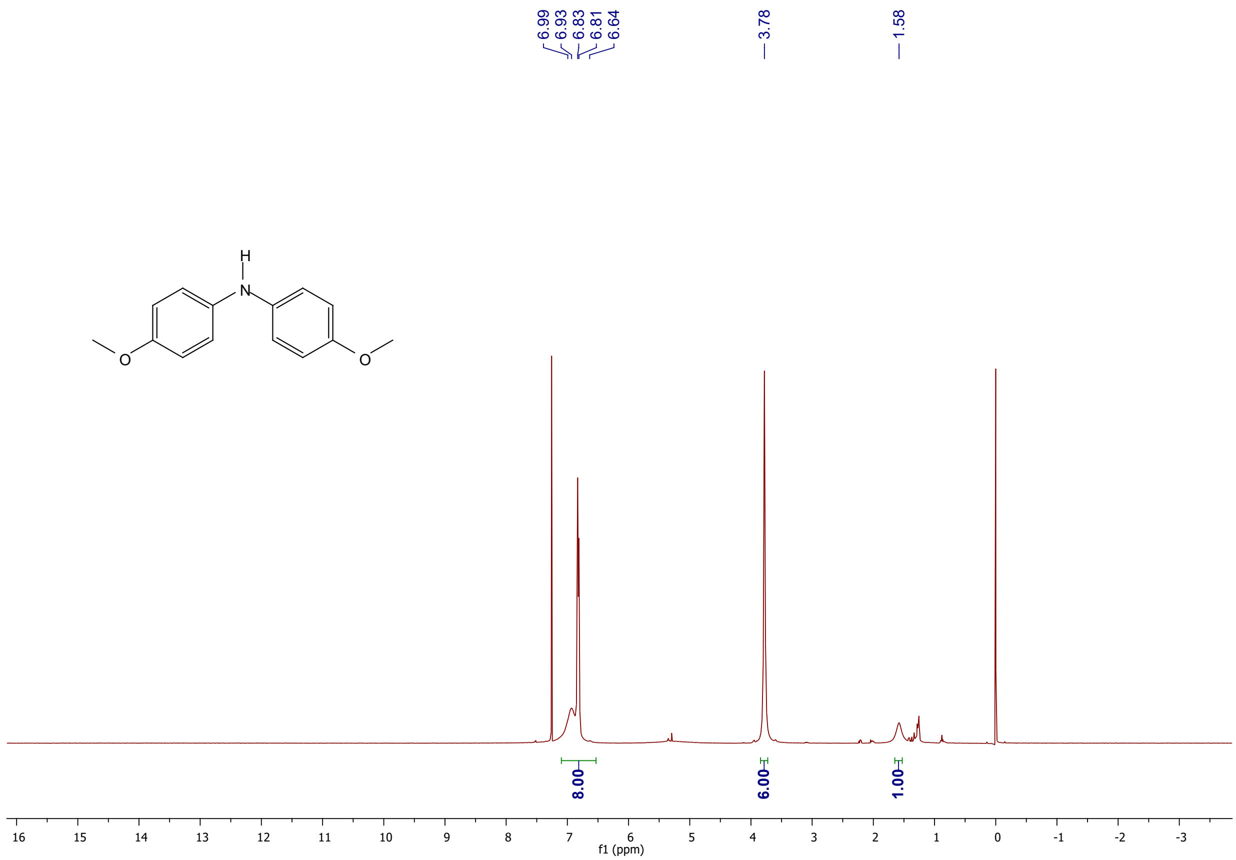

7.22
7.21
7.19
7.17
7.09
7.07
6.89
6.87
6.79
6.77
6.76
3.80
3.33
3.31
3.24
3.22
CH3
N
H3C
O
2.07
1.96
4.98
3.00
3.00
f1 (ppm)

4g



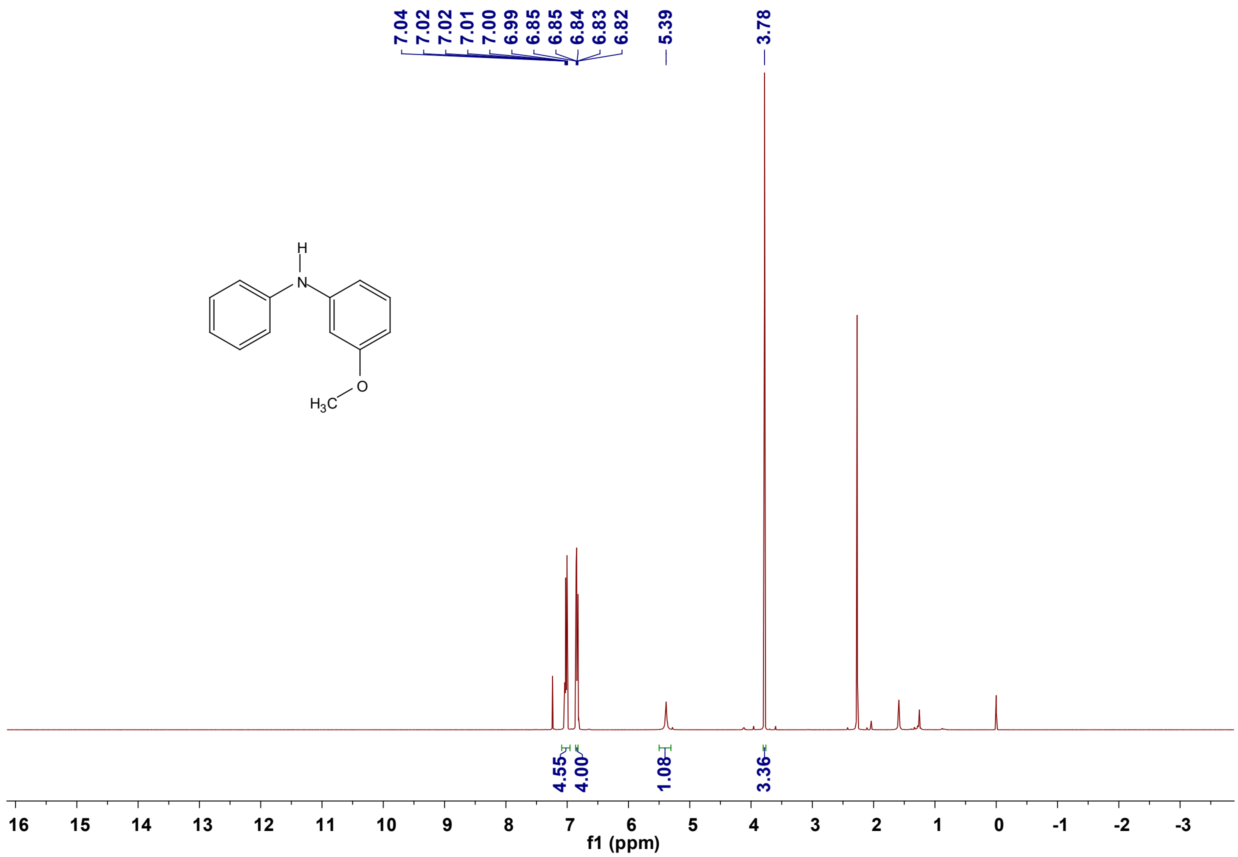
8.30
8.30
8.12
8.11
7.29
7.21
7.19
7.12
7.10
7.07
7.03
3.30
3.30
3.30
CH3
N
N
0.97
0.98
2.02
4.91
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4h

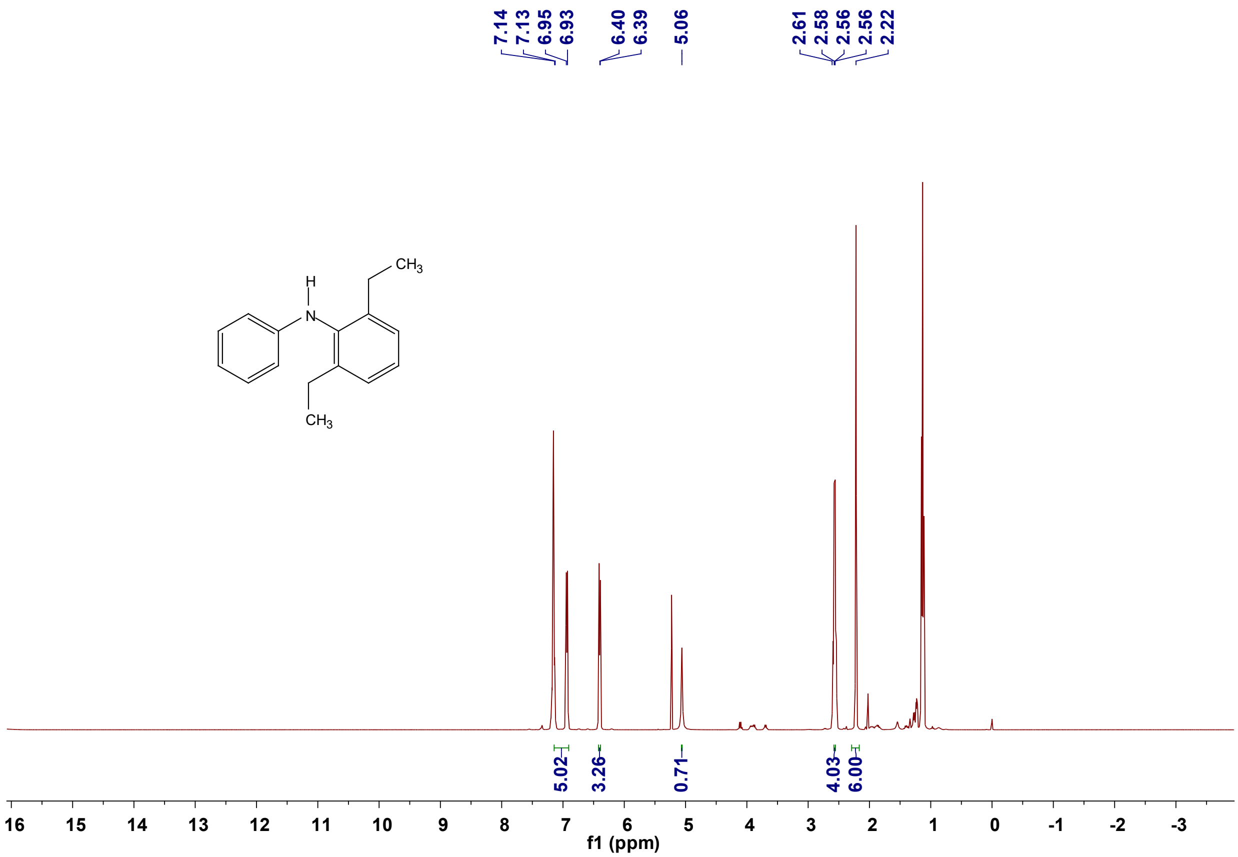


6.99
6.93
6.83
6.81
6.64
3.78
1.58
H
N
O
O
8.00
6.00
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

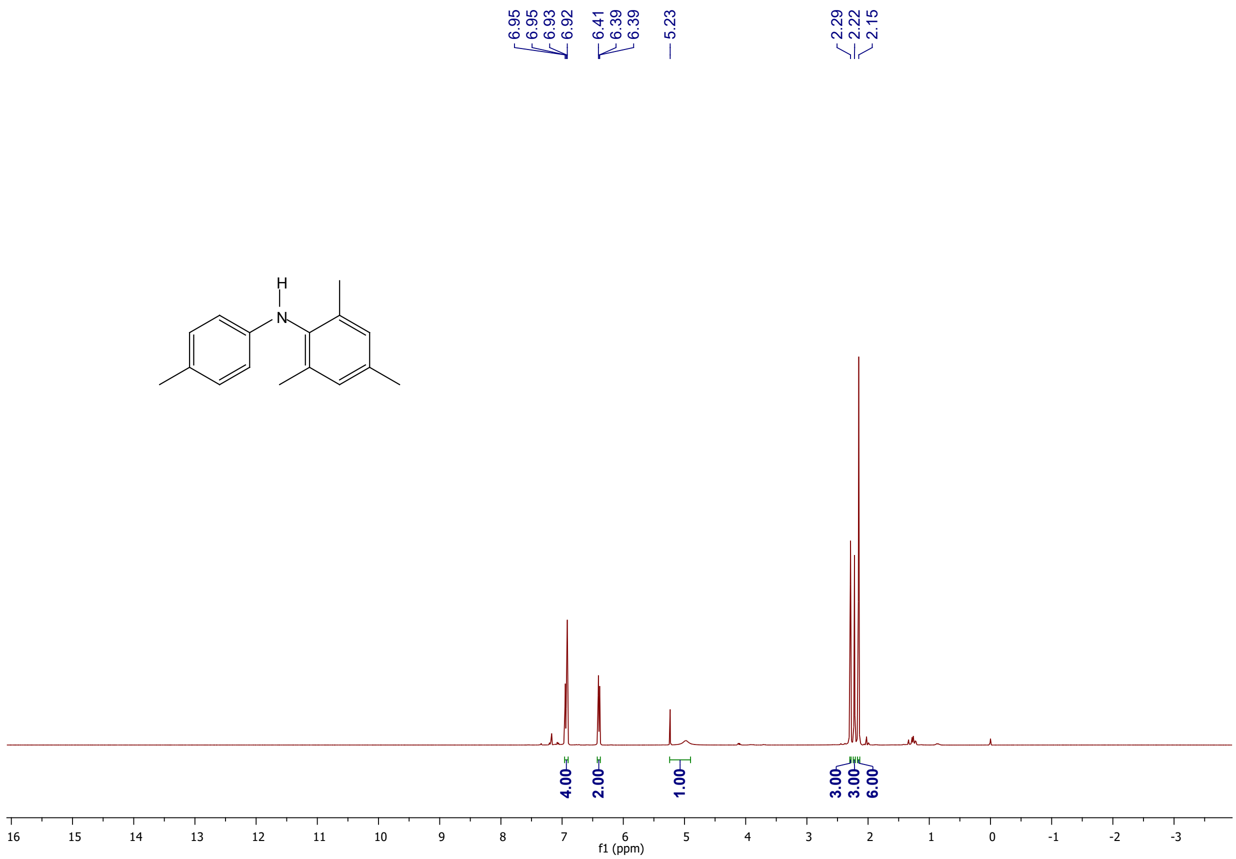
4i


7.04
7.02
7.02
7.01
7.00
6.99
6.85
6.85
6.84
6.83
6.82
5.39
3.78
H
N
O
H3C
4.55
4.00
1.08
3.36
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4j

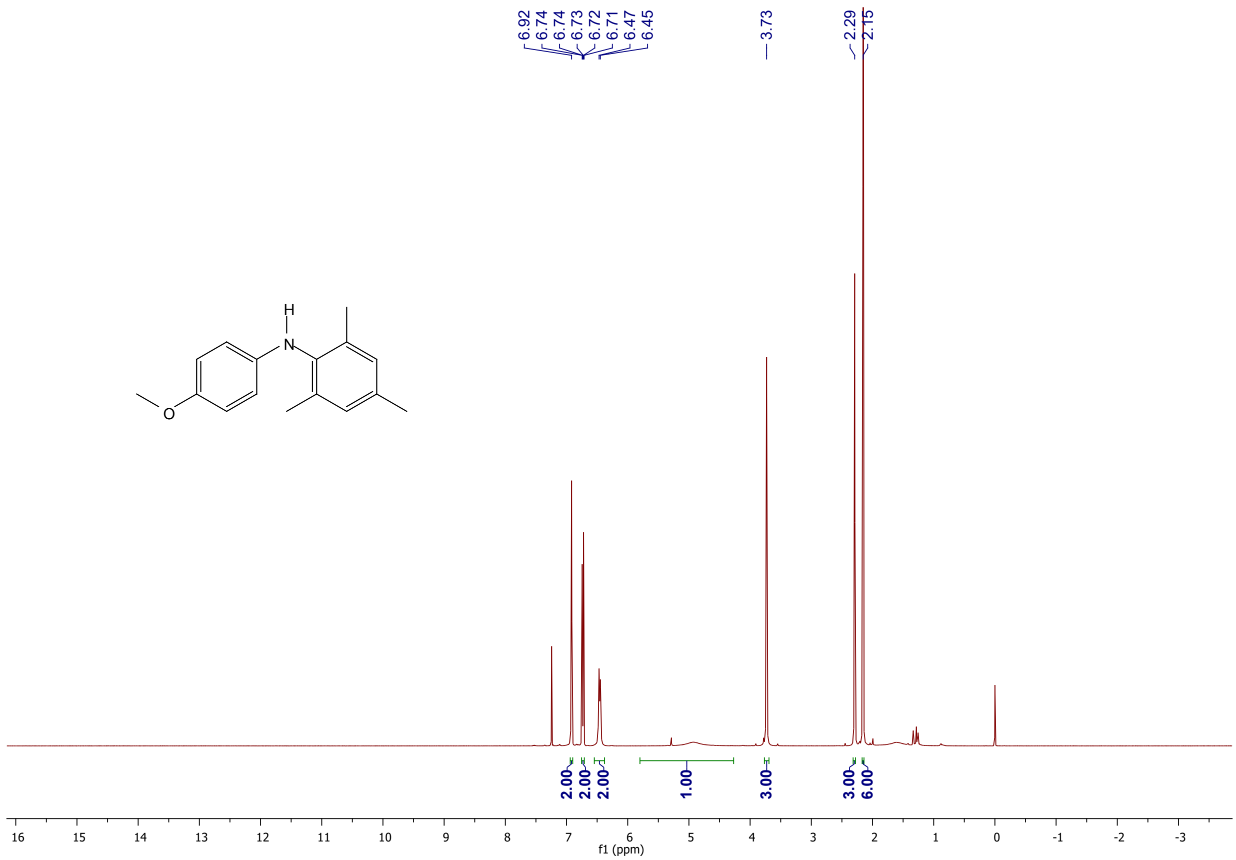

7.14
7.13
6.95
6.93
6.40
6.39
5.06
2.61
2.58
2.56
2.56
2.22
H
N
CH3
CH3
5.02
3.26
0.71
4.03
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4k

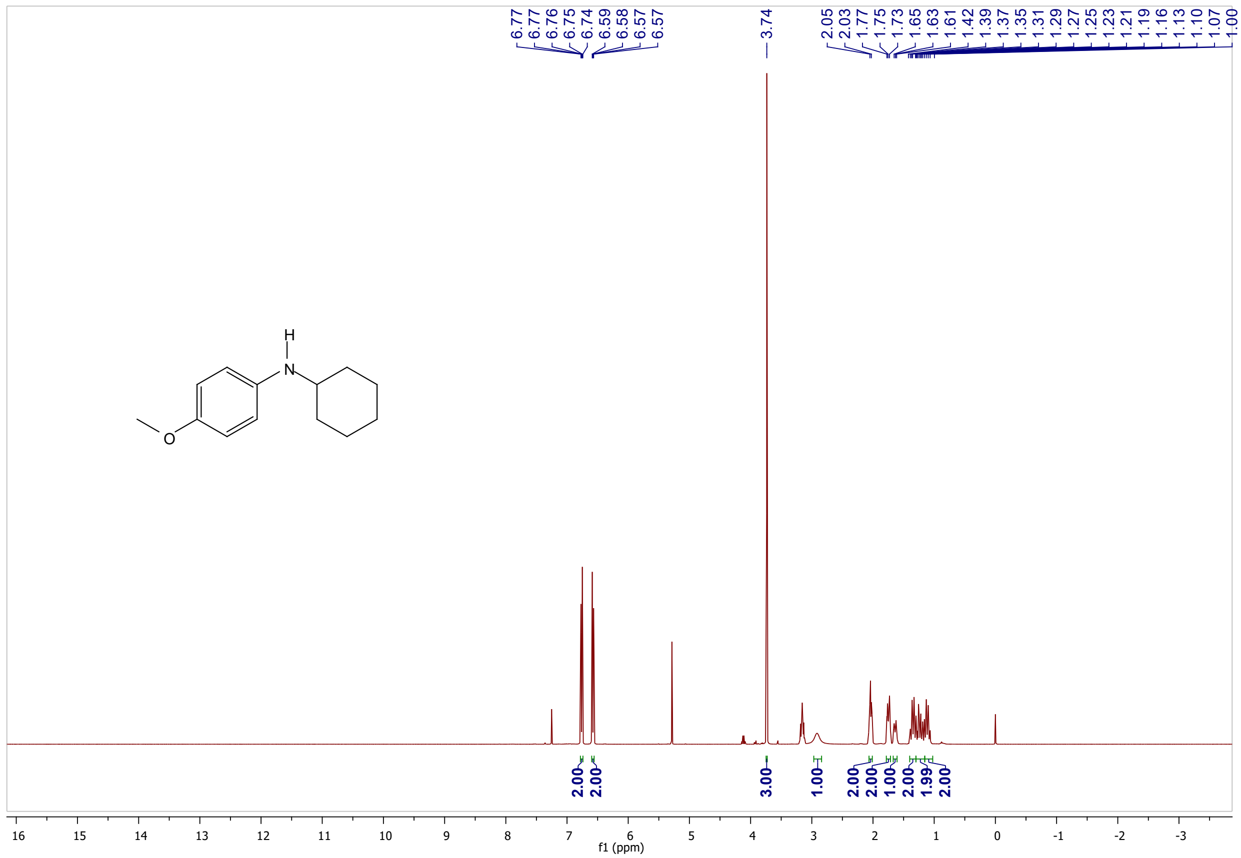


6.95
6.95
6.93
6.92
6.41
6.39
6.39
5.23
2.29
2.22
2.15
4.00
2.00
1.00
3.00
3.00
6.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

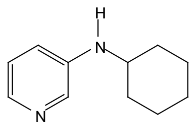
4l

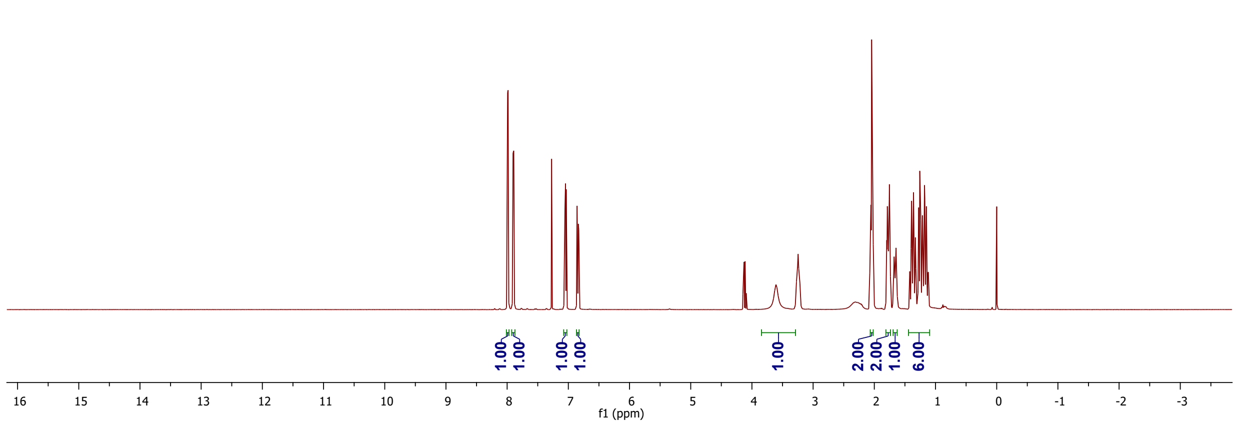

6.92
6.74
6.74
6.73
6.72
6.71
6.47
6.45
3.73
2.29
2.15
H
N
O
2.00
2.00
2.00
1.00
3.00
3.00
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4m


6.77
6.77
6.76
6.75
6.74
6.59
6.58
6.57
6.57
3.74
2.05
2.03
1.77
1.75
1.73
1.65
1.63
1.61
1.42
1.39
1.37
1.35
1.31
1.29
1.27
1.25
1.23
1.21
1.19
1.16
1.13
1.10
1.07
1.00
H
N
O
2.00
2.00
3.00
1.00
2.00
2.00
1.00
2.00
1.99
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

4n




7.99
7.98
7.90
7.89
6.86
6.85
6.85
6.84
6.84
6.83
6.83
3.61
2.04
1.42
1.41
1.40
1.39
1.36
1.33
1.33
1.32
1.30
1.28
1.28
1.27
1.26
1.24
1.24
1.22
1.21
1.20
1.18
1.15
1.13
1.12
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
6.00
f1 (ppm)