Carboxylic Acids as Double Aryl Group Donors for Biaryl Synthesis

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been previously described in literature or prepared by the method reported previously. Phenylboronic acid were prepared by standard methods. All experiments involving palladium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by ^{1}H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.26 and 77.03 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (*J*) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all compounds in the Supporting Experimental. ^{1}H NMR, and ^{13}C NMR data are reported for all new compounds.

Experimental Procedures and Characterization Data

General Procedure for Decarbonylative Borylation of Carboxylic Acids. An oven-dried vial equipped with a magnetic stir bar was charged with carboxylic acid (1.0 equiv), bis(pinacolato)diboron (1.5 equiv), $Pd(OAc)_2$ (typically, 3 mol%), ligand (typically, 6 mol%), 4-dimethyl-aminopyridine (1.5 equiv) and trimethylacetic anhydride (1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Representative Procedure for Decarbonylative Borylation of Carboxylic Acids. An oven-dried vial equipped with a magnetic stir bar was charged with benzoic acid (244 mg, 2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (762 mg, 1.5 equiv), $Pd(OAc)_2$ (14 mg, 3 mol%), 1,3-bis(diphenyl-phosphino)propane (52 mg, 6 mol%), 4-dimethylaminopyridine (366 mg, 1.5 equiv) and trimethylacetic anhydride (558 mg, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10 mL), filtered, and concentrated. Purification by chromatography on silica gel (CH_2Cl_2/petroleum ether) afforded the title product. Yield 98% (400.0 mg). White solid. Characterization data are included in the section below.

General Procedure for Hydrolysis of Boronic Esters. A round-bottom flask equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (1.0 equiv) and THF/H_2O (4:1, 10 mL), the $NaIO_4$ (8.0 equiv) was added. The suspension was stirred for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature.

Representative Procedure for Hydrolysis of Boronic Esters. A round-bottom flask equipped with a magnetic stir bar was charged with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (neat, 204.1 mg, 1.0 mmol, 1.0 equiv) and THF/H_2O (4:1, 10 mL), the $NaIO_4$

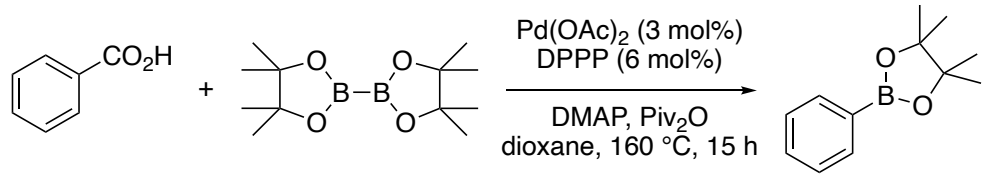
(1.71 g, 8.0 mmol, 8.0 equiv) was added. The suspension was stirred for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature. After the indicated time, the reaction mixture was diluted with water (10 mL) and extracted with EtOAC (3×30 mL). The combined organic phases were washed with brine (30 mL) and water (30 mL), dried, filtered, and concentrated. Purification by chromatography on silica gel (ethyl acetate/petroleum ether) afforded the title product. Yield 69% (84.1mg). White solid. Characterization data are included in the section below.

General Procedure for Decarbonylative Suzuki-Miyaura Coupling of Carboxylic Acids. An oven-dried vial equipped with a stir bar was charged with carboxylic acid (neat, 0.2 mmol, 1.0 equiv), aryl boronic acid (neat, 2.0 equiv), $Pd(OAc)_2$ (typically, 3 mol%), ligand (typically, 6 mol%), *N,N*-diisopropylethylamine (typically, 2.0 equiv), boric acid (2.0 equiv) and trimethylacetic anhydride (2.0 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C.

Representative Procedure for Decarbonylative Suzuki-Miyaura Coupling of Carboxylic Acids. An oven-dried vial equipped with a stir bar was charged with 3-pyridinecarboxylic acid (neat, 24.6 mg, 0.2 mmol, 1.0 equiv), 4-tolylboronic acid (neat, 54.4 mg, 0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol, 3 mol%), 1,3-bis(diphenylphosphino)propane (5.0 mg, 0.012 mmol, 6 mol%), *N,N*-diisopropylethylamine (51.6 mg, 0.4 mmol, 2.0 equiv), boric acid (24.8 mg, 0.4 mmol, 2.0 equiv) and trimethylacetic anhydride (74.4 mg, 0.4 mmol, 2.0 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Dioxane (0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with CH_2Cl_2 (10.0 mL), filtered, and concentrated. Purification by chromatography on silica gel (ethyl acetate/hexane) afforded the title product. Yield 96% (32.5 mg). White solid. Characterization data are included in the section below.

Characterization Data of Aryl Boronic Esters

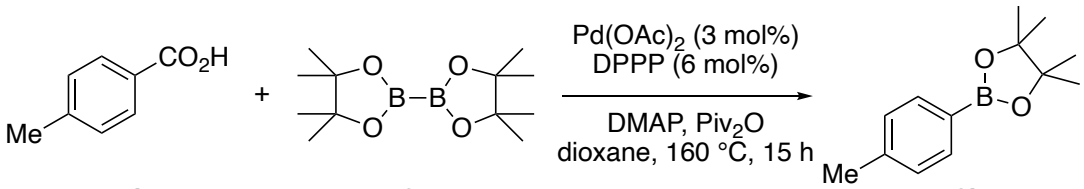
4,4,5,5- Tetramethyl-2-phenyl-1,3,2-dioxaborolane (Scheme 1, 3a)[1]



1a **2a** **3a**

According to the general procedure, the reaction of benzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenyl-phosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (400.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83-7.81 (d, *J* = 7.5 Hz, 2H), 7.39-7.36 (m, 1H), 7.24-7.23 (m, 2H), 1.23 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 134.75, 131.27, 127.72, 83.78, 24.88.

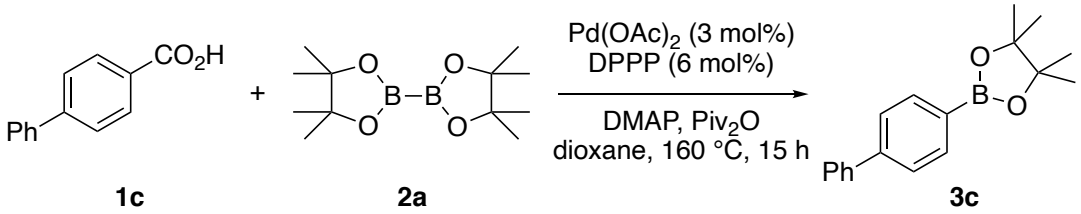
4,4,5,5-Tetramethyl-2-(4-methylphenyl)-1,3,2-dioxaborolane (Scheme 1, 3b)[2]



1b **2a** **3b**

According to the general procedure, the reaction of 4-methylbenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol,1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenyl-phosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol,1.5 equiv) and trimethyl acetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 78% yield (340.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71-7.69 (d, *J* = 7.9 Hz, 2H), 7.20-7.18 (d, *J* = 7.6 Hz, 2H), 2.36 (s,3H), 1.34 (s,12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.42,134,81,128.54, 83.63, 25.04, 21.74.

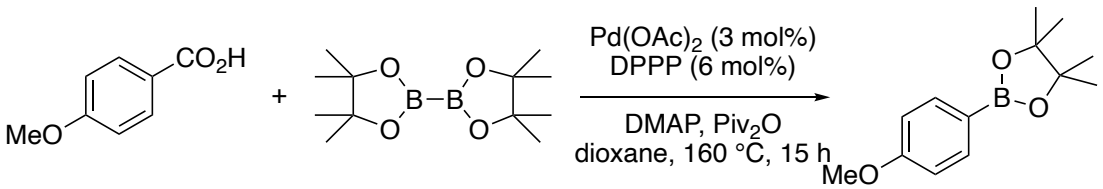
2-(4-Biphenylyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3c)[1]



1c **2a** **3c**

According to the general procedure, the reaction of 4-phenylbenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenyl-phosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol,1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 88% yield (493.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.90-7.88(m, 2H), 7.64-7.61 (m,4H), 7.47-7.43 (t, *J* = 7.5 Hz, 2H), 7.38-7.34 (t, *J* = 8.0 Hz, 1H), 1.37 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.90, 141.02, 135.26, 128.78, 127.57, 127.25, 126.48, 83.84, 24.89.

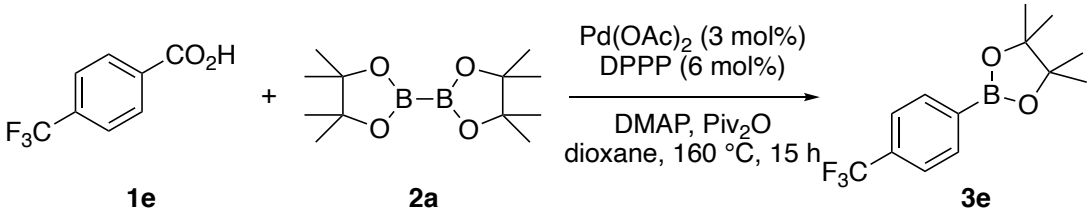
2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3d)[1]



1d **2a** **3d**

According to the general procedure, the reaction of 4-methoxybenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenyl-phosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol,1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (299.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 -7.75 (d, *J* = 10.8 Hz,2H), 6.91-6.89 (d, *J* = 6.8 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.14, 136.52, 113.31, 83.56, 55.10, 27.87.

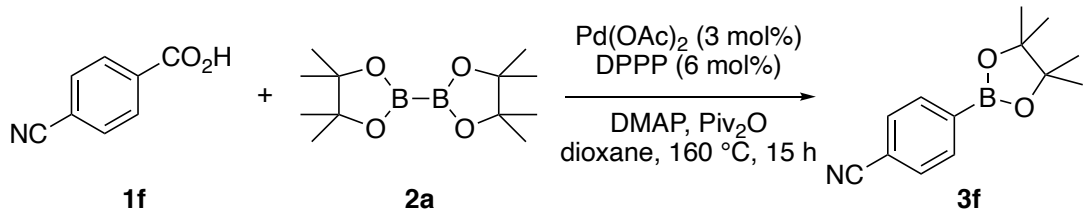
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (Scheme 1, 3e)[1]



1e **2a** **3e**

According to the general procedure, the reaction of 4-(trifluoromethyl) benzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3,0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis-(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (522.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.90 (d, *J* = 7.8 Hz 2H), 7.62-7.60 (d, *J* = 7.8 Hz, 2H), 1.36 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 135.02, 132.83 (q, J^F= 32 Hz), 124.33 (q, J^F= 4 Hz), 124.15 (q, J^F= 270 Hz), 84.28, 24.87. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.02.

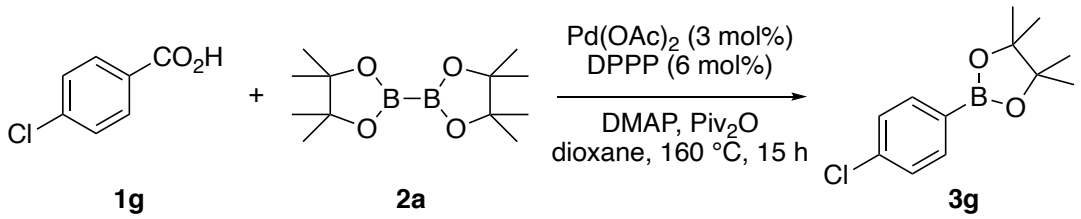
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (Scheme 1, 3f)[1]



1f **2a** **3f**

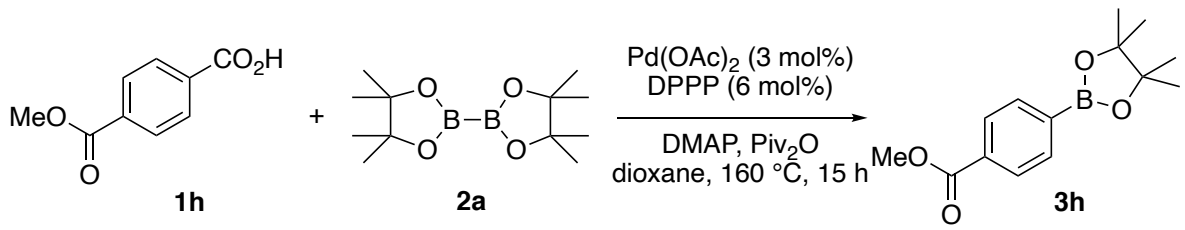
According to the general procedure, the reaction of 4-cyanobenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis (diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (421.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89-7.87(d, *J* = 8.2 Hz, 2H), 7.65-7.63 (d, *J* = 8.3 Hz, 2H), 1.35 (s, 12H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 135.11, 131.16, 118.90 114.54, 84.51, 24.88.

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3g)[1]



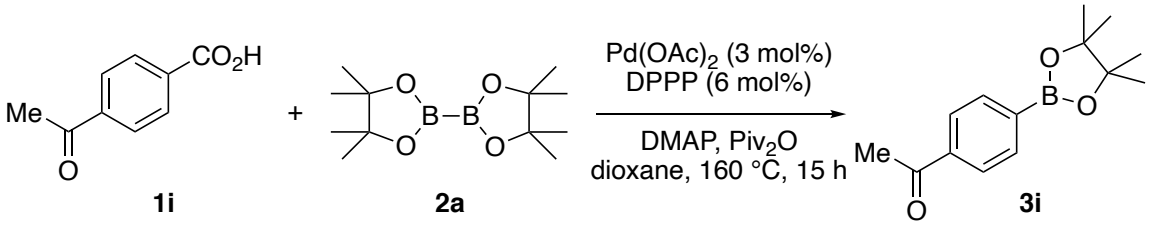
According to the general procedure, the reaction of 4-chlorobenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenyl-phosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethyl acetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 89% yield (423.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74-7.72 (d, *J* = 8.3 Hz, 2H), 7.35-7.33 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 137.54, 136.13, 128.02, 84.02, 24.87.

Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (Scheme 1, 3h)[1]



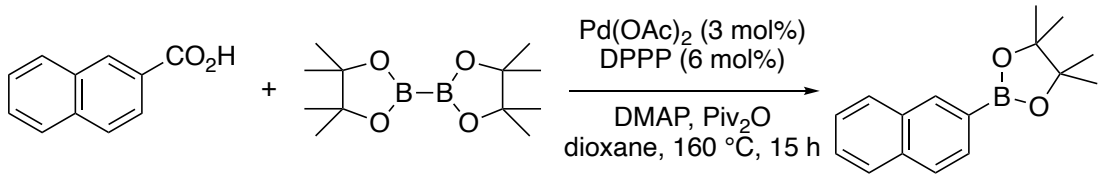
According to the general procedure, the reaction of mono-methyl terephthlate (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (561.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03-8.01 (d, *J* = 8.3 Hz, 2H), 7.88-7.86 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.16, 134.67, 132.30, 128.61, 84.19, 52.18, 24.90.

4-Acetylphenylboronic acid pinacol ester (Scheme 1, 3i)[1]



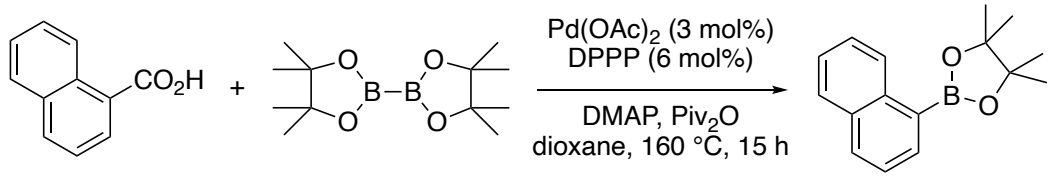
According to the general procedure, the reaction of 4-acetylbenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino) propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (452.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.94-7.92 (d, *J* = 8.4 Hz, 2H), 7.90-7.88 (d, *J* = 8.3 Hz, 2H), 2.62 (s, 3H), 1.36 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 198.52, 139.00, 134.94, 127.31, 84.24, 26.81, 24.90.

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (Scheme 1, 3j)[1]



According to the general procedure, the reaction of 2-naphthoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 81% yield (411.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.37 (s, 1H), 7.90 (s, 1H), 7.82 (s, 3H), 7.53- 7.45 (m, 2H), 1.40 (s, 12H). **^{13}C NMR (100MHz, $CDCl_3$)** δ 136.26, 135.04, 132.82, 130.41, 128.68, 127.72, 126.99, 125.81, 83.95, 24.95.

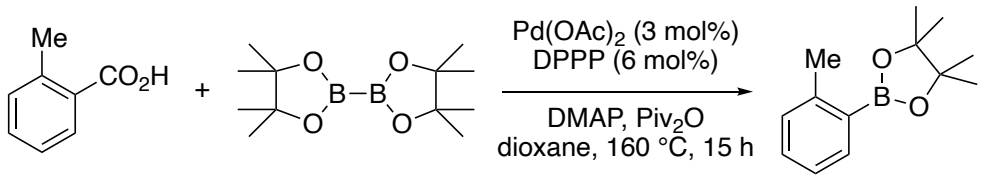
Naphthalene-1-boronic acid pinacol ester (Scheme 1, 3k)[2]



1k **2a** **3k**

According to the general procedure, the reaction of 1-naphthoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino) propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (442.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78-8.76 (d, *J* = 8.4 Hz, 1H), 8.09-8.07 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.95-7.93 (d, *J* = 8.2 Hz, 1H), 7.85-7.83 (d, *J* = 8.5 Hz, 1H), 7.56-7.52 (m, 1H), 7.49-7.46(m, 2H), 1.43 (s, 12H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 136.92, 135.65, 133.20, 131.62, 128.41, 128.35, 126.35, 125.49, 124.97, 83.75, 24.98.

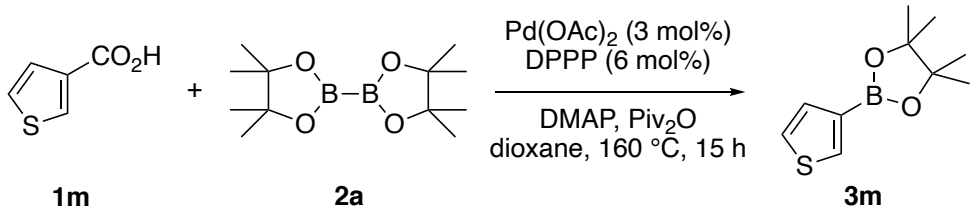
4,4,5,5-Tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (Scheme 1, 3l)[1]



1l **2a** **3l**

According to the general procedure, the reaction of 2-methylbenzoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 80% yield (349.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76-7.75 (dd, *J* = 7.7,1.6 Hz, 1H), 7.34-7.30 (td, *J* = 7.5,1.6 Hz, 1H), 7.17-7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.83, 135.86, 130.79, 129.77, 124.70, 83.39, 24.89, 22.23.

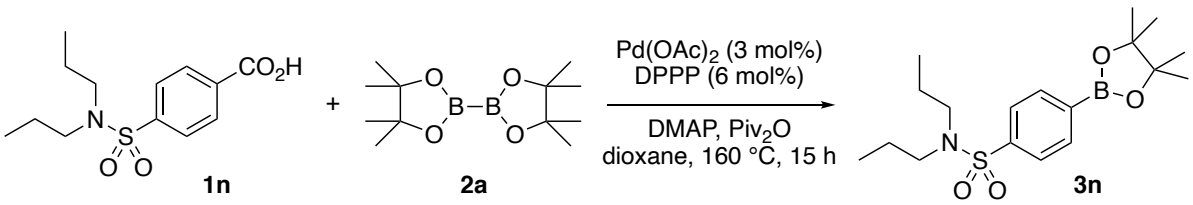
4,4,5,5-Tetramethyl-2-thiophen-3-yl-[1,3,2]dioxaborolane (Scheme 1, 3m)[1]



1m **2a** **3m**

According to the general procedure, the reaction of 3-thiophenezoic acid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol,1.5 equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (256.2 mg). White solid**.** **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93-7.92 (d, *J* = 3.6 Hz, 1H), 7.42-7.40 (d, *J* = 4.0 Hz, 1H), 7.35-7.33 (m, 1H), 1.34 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 136.47, 132.03, 125.35,83.67, 24.85.

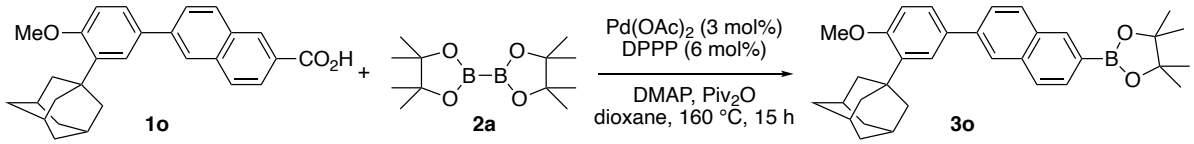
***N,N*-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (Scheme 1, 3n)[1]**



1n **2a** **3n**

According to the general procedure, the reaction of probenecid (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethylacetic anhydride (3.0 mmol, 1.5e quiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatograph the title compound in 97% yield (712.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.90 (d, *J* = 8.3 Hz, 2H), 7.78-7.76 (d, *J* = 8.3 Hz, 2H), 3.08-3.04 (t, *J* = 8.0 Hz,4H), 1.55-1.47 (m, 4H), 1.35 (s, 12H), 0.87-0.83 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 142.31, 135.21, 126.01, 84.36, 49.93, 24.86, 21.92, 11.16.

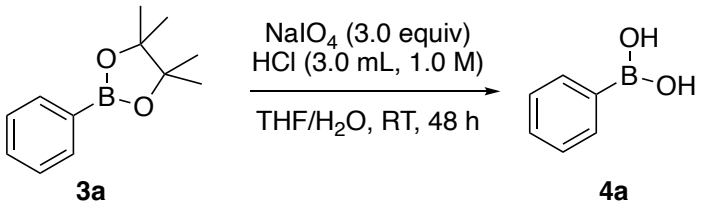
2-(6-(3-((3r,5r,7r)-Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Scheme 1, 3o)[3]



According to the general procedure, the reaction of adapalene (2.0 mmol, 1.0 equiv), bis(pinacolato)diboron (3.0 mmol, 1.5 equiv), $Pd(OAc)_2$ (3 mol%), 1,3-bis(diphenylphosphino)propane (6 mol%), 4-dimethylaminopyridine (3.0 mmol, 1.5 equiv) and trimethyl acetic anhydride (3.0 mmol, 1.5equiv) in 1,4-dioxane (10.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 53% yield (524.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 8.05-8.03 (t, *J* = 4.0 Hz 2H), 7.97 (s, 2H), 7.86-7.83 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.57-7.55 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.02-7.00 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.18 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H), 1.25 (s, 12H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.13, 139.13, 136.97, 134.38, 133.79, 132.33,131.38, 129.92, 129.18, 126.90, 126.03, 125.82, 125.04, 123.19, 112.16, 84.73,55.20, 40.62, 37.13, 29.12, 25.96.

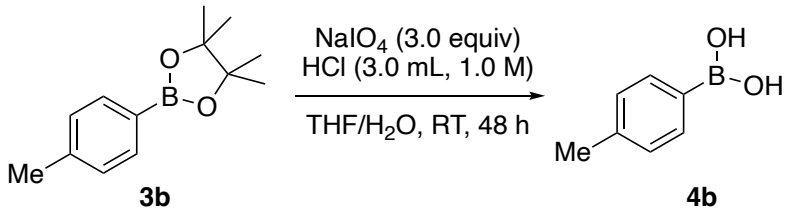
Characterization Date for Hydrolysis of Aryl Boronic Esters

Phenylboronic acid (Scheme 2, 4a)[2]



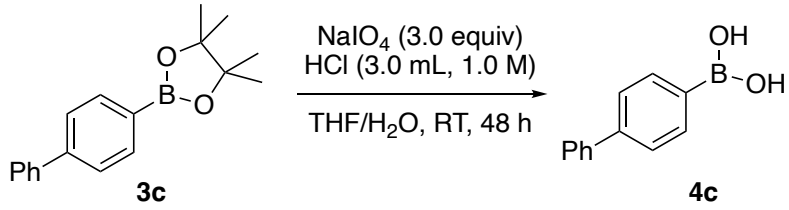
According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 69% yield (84.1 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.91-7.89 (dd, *J* = 6.8, 2.5 Hz, 2H), 7.40-7.36 (m, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 133.50, 129.52, 127.50.

4-Tolylboronic acid (Scheme 2, 4b)[2]



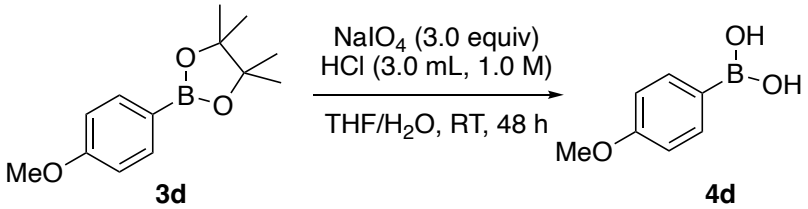
According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-(4-methylphenyl)-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 86% yield (116.5 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.77-7.76 (d, *J* = 7.7 Hz, 2H), 7.19-7.17 (d, *J* = 7.7 Hz, 2H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 138.66, 133.57, 128.14, 21.26.

4-Biphenylboronic acid (Scheme 2, 4c)[4]



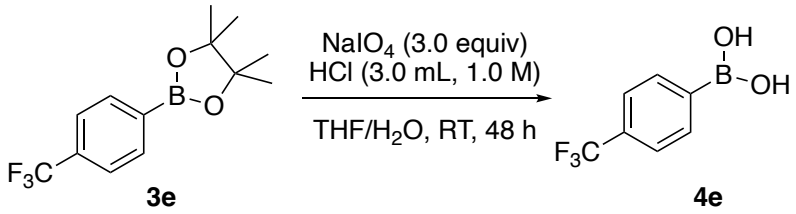
According to the general procedure, the reaction of 2-(4-biphenylyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 84% yield (166.2 mg). White solid**.** **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.93-7.91 (d, *J* = 8.0 Hz, 2H), 7.69-7.63 (dd, *J* = 15.6, 7.7 Hz, 4H), 7.48-7.44 (t, *J* = 7.6 Hz, 2H), 7.38-7.34 (t, *J* = 7.3 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 141.69, 140.21, 134.90, 129.01, 127.64, 126.79, 125.76.

4-Methoxyphenyl-boronic acid (Scheme 2, 4d)[2]



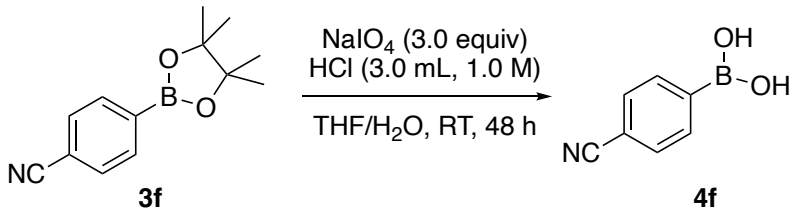
According to the general procedure, the reaction of 2-(4-methoxyphenyl)-4,4,5,5-tetra-methyl-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 75% yield (113.4 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.77-7.75 (d, *J* = 8.6 Hz, 2H), 6.90-6.88 (d, *J* = 8.6 Hz, 2H), 3.75(s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 161.05, 135.98, 113.04, 54.92.

(4-(Trifluoromethyl)phenyl)boronic acid (Scheme 2, 4e)[2]



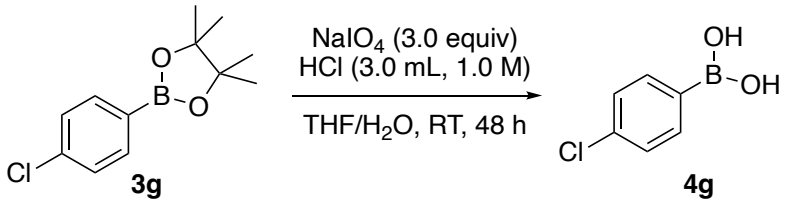
According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-(4-(trifluoromethyl) phenyl)-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 78% yield (148.2 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.01-7.99 (d, *J* = 7.8 Hz, 2H), 7.68-7.66 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 134.79, 130.34 (q, J^F= 31 Hz), 124.48 (q, J^F= 270 Hz), 123.99 (q, J^F= 4.0 Hz). **^{19}F NMR (376 MHz, DMSO)** δ -63.02.

4-Cyanophenylboronic acid (Scheme 2, 4f)[2]



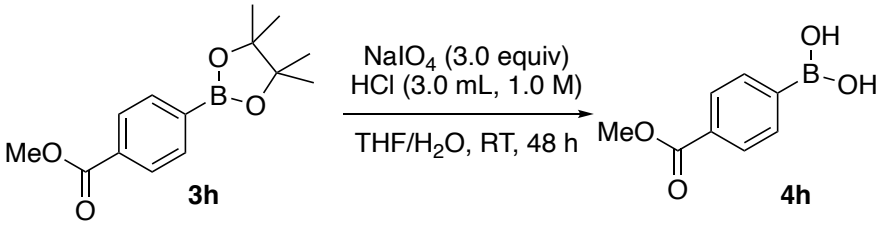
According to the general procedure, the reaction of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 84% yield (123.1 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.07-8.05 (d, *J* = 8.6 Hz, 2H), 7.95-7.93 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 132.72, 130.00, 118.26, 115.16.

4-Chlorophenylboronic acid (Scheme 2, 4g)[2]



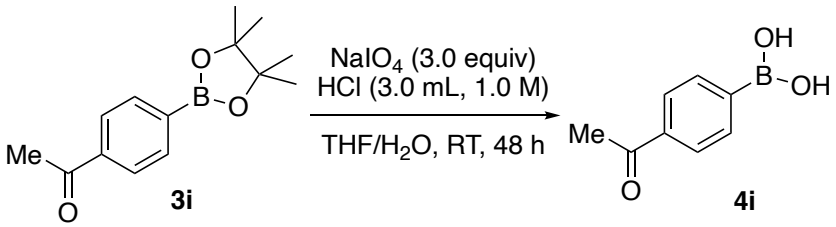
According to the general procedure, the reaction of 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 68% yield (105.7 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.88-7.86 (d, *J* = 8.1 Hz, 2H), 7.44-7.42 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 136.02, 135.30, 127.60.

4-(Methoxycarbonyl)phenylboronic acid (Scheme 2, 4h)[5]



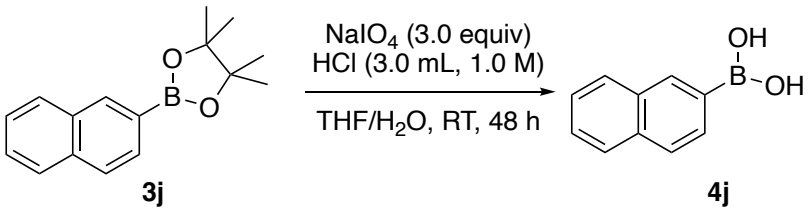
According to the general procedure.the reaction of methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 76% yield (136.7 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.91 (s, 4H), 3.84 (s, 3H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 166.46, 134.32, 130.82, 128.01, 52.15.

(4-Acetylphenyl)boronic acid (Scheme 2, 4i)[6]



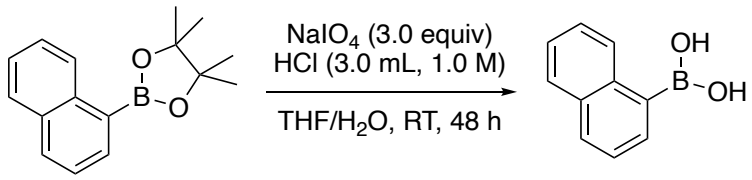
According to the general procedure. the reaction of 4-acetylphenylboronic acid pinacol ester (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 74% yield (121.4 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.92-7.91 (d, *J* = 1.9 Hz, 4H), 2.57 (s, 3H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 198.35, 137.93, 134.35, 127.06, 26.88.

2-Naphthaleneboronic acid (Scheme 2, 4j)[7]



According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 98% yield (168.5 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.39 (s, 1H), 8.21 (s, 2H), 7.92-7.84 (dt, *J* = 17.6, 9.0 Hz, 4H), 7.53-7.49 (m, 2H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 134.99, 134.06, 132.46, 130.66, 128.37, 127.51, 126.63, 126.42, 125.79.

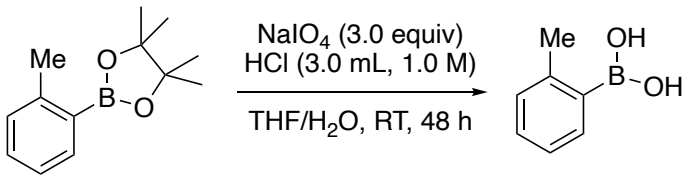
Naphthalene-1-boronic acid pinacol ester (Scheme 2, 4k)[8]



3k **4k**

According to the general procedure, the reaction of naphthalene-1-boronic acid pinacol ester 1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 82% yield (141.2 mg). White solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.42-8.40 (d, J = 7.7 Hz, 1H), 7.92- 7.88 (m, 2H), 7.78-7.76 (dd, J = 6.7, 1.0 Hz, 1H), 7.52-7.47 (tt, J = 6.8, 3.5 Hz, 3H). **^{13}C NMR (100MHz, DMSO-d_6)** δ 135.66, 132.91, 132.10, 129.21, 128.80, 128.27, 125.69, 125.42, 125.14.

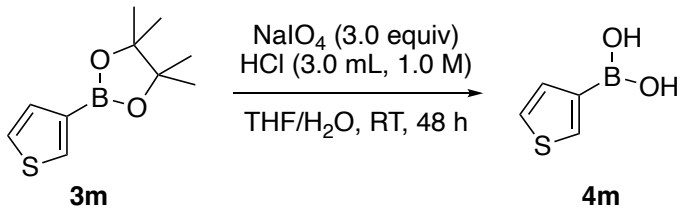
2-Methylphenylboronic acid (Scheme 2, 4l)[9]



3l **4l**

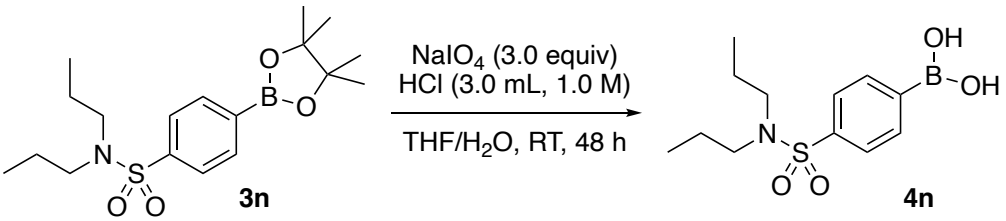
According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 83% yield (112.7 mg). White solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.92-7.90 (d, J = 7.3 Hz, 1H), 7.28-7.22 (m, 1H), 7.20-7.09 (dt, J = 12.9, 7.1 Hz, 2H), 2.67 (s, 3H). **^{13}C NMR (100MHz, DMSO-d_6)** δ 143.33, 134.73, 129.87, 129.21, 124.64, 22.37.

3-Thiopheneboronic acid (Scheme 2, 4m)[8]



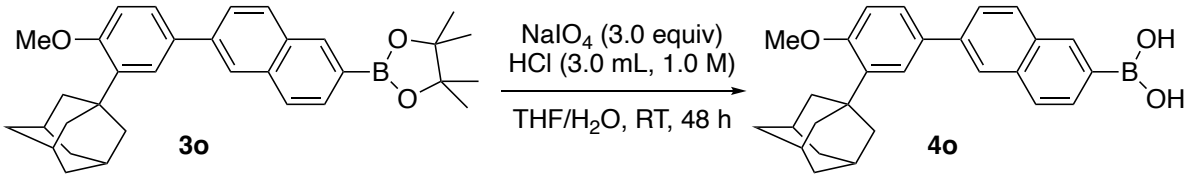
According to the general procedure, the reaction of 4,4,5,5-tetramethyl-2-thiophen-3-yl-[1,3,2]dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 90% yield (115.3 mg). White solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.01 (s, 2H), 7.97-7.96 (m, 1H), 7.48-7.46 (dd, *J* = 4.8, 2.7 Hz, 1H), 7.42- 7.41 (m, 1H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 134.95, 132.52, 125.19.

(4-(*N*,*N*-dipropylsulfamoyl)phenyl) boronic acid (Scheme 2, 4n)[10]



According to the general procedure, the reaction of *N,N*-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 70% yield (199.5 mg). Yellow solid. **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.36 (s, 2H), 7.97-7.95 (d, *J* = 8.2 Hz, 2H), 7.75-7.73 (d, *J* = 8.3 Hz, 2H), 3.03-2.99 (m, 4H), 1.50-1.40 (m, 4H), 0.82-0.78 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100MHz, DMSO-*d*$_6$)** δ 140.67, 134.79, 125.58, 49.66, 21.65, 11.02.

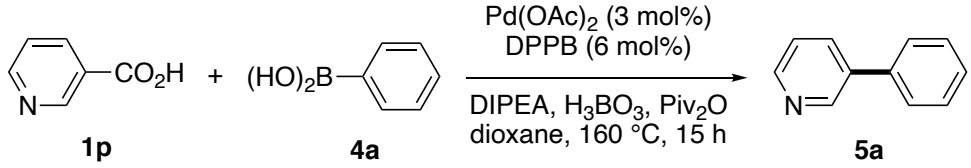
(6-(3-((3r,5r,7r)-Adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)boronic acid (Scheme 2, 4o)[11]



According to the general procedure, the reaction of 2-(6-(3-((3r,5r,7r)-adamantan-1-yl) -4-methoxy-phenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.0 mmol, 1.0 equiv), $NaIO_4$ (8.0 equiv) in THF/H_2O (4:1, 10 mL) for 40 min at room temperature, then HCI (1.0 M, 1.5 mL) was added, the mixture was stirred for 48 h at room temperature, afforded after work-up and chromatography the title compound in 62% yield (255.2 mg). White solid. **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.59 (s, 1H), 8.22 (s, 1H), 8.16-8.14 (d, J = 8.7 Hz, 1H), 8.08-8.06 (d, J = 8.7 Hz, 1H), 7.99-7.96 (dd, J = 8.6, 1.5 Hz, 1H), 7.90-7.87 (dd, J = 8.6, 1.6 Hz, 1H), 7.67-7.64 (dd, J = 8.5, 2.2 Hz, 1H), 7.58 -7.57 (d, J = 2.2 Hz, 1H), 7.13-7.11 (d, J = 8.6 Hz, 1H), 3.87 (s, 3H), 2.14 (s, 6H), 2.07 (s, 3H), 1.76 (s, 6H). **^{13}C NMR (100MHz, DMSO-d_6)** δ 158.44, 140.07, 137.89, 135.32, 131.35, 130.75, 130.10, 129.69, 128.20, 125.80, 125.61, 125.33, 124.93, 123.92, 112.55, 55.19, 36.39, 28.23, 18.13.

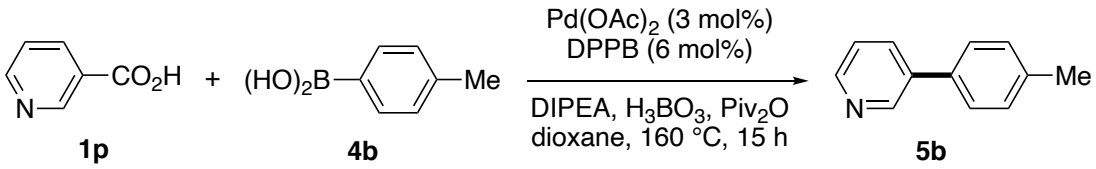
Characterization Date for Suzuki of Carboxylic Acids and Boronic Acids

3-Phenylpyridine (Scheme 3, 5a)[12]



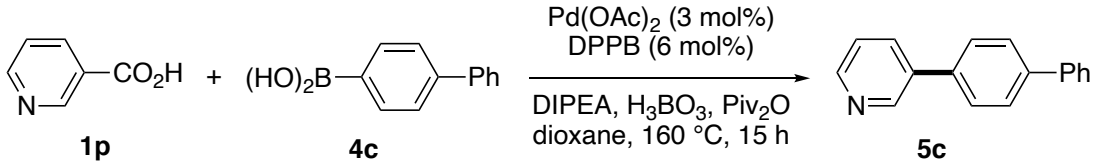
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 82% yield (25.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (s, 1H), 8.62 (s, 1H), 7.93-7.91 (d, *J* = 11.8 Hz, 1H), 7.60-7.58 (d, *J* = 5.0 Hz, 2H), 7.51-7.47 (t, *J* = 7.4 Hz, 2H), 7.43-7.39 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.02, 147.94, 137.55, 134.95, 129.13, 128.26, 127.18, 123.82.

3-(p-Tolyl)pyridine (Scheme 3, 5b)[13]



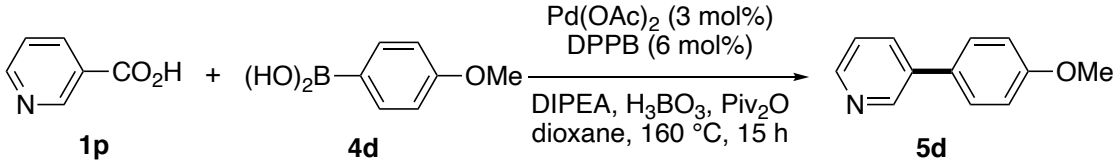
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-tolylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (32.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.85 (s, 1H), 8.58 -8.57 (d, *J* = 4.0 Hz, 1H), 7.88-7.87 (d, *J* = 4.0 Hz, 1H), 7.50-7.48 (d, *J* = 8.0 Hz, 2H), 7.38-7.35 (q, *J* = 4.0 Hz,1H), 7.30-7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.93, 138.13, 136.74, 134.83, 134.40, 129.84, 129.35,127.00, 123.64, 21.16.

3-([1,1'-Biphenyl]-4-yl)pyridine (Scheme 3, 5c)[13]



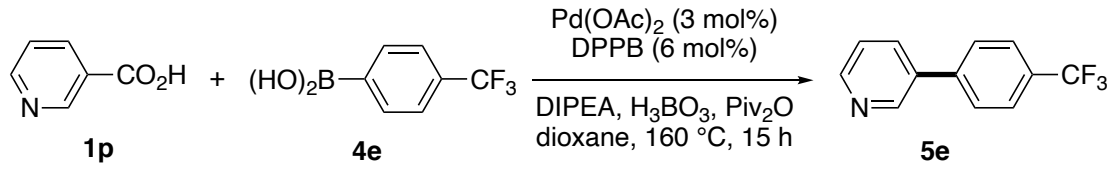
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-biphenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (42.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.92 (s, 1H), 8.62 (s, 1H), 7.94-7.92 (d, *J* = 9.8 Hz, 1H), 7.73-7.71 (d, *J* = 8.5 Hz, 2H), 7.68-7.74 (m, 4H), 7.50-7.46 (t, *J* = 7.5 Hz, 2H), 7.41-7.37 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.45, 148.17, 141.05, 140.38, 136.66, 136.24, 134.30, 130.72, 128.91, 127.83, 127.52, 127.09, 123.66.

3-(4-Methoxyphenyl)- pyridine (Scheme 3, 5d)[12]



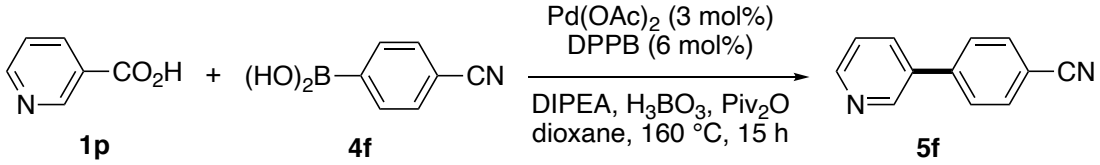
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-methoxyphenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (32.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 8.56 (s, 1H), 7.85-7.83 (d, *J* = 8.2 Hz, 1H), 7.54-7.51 (m, 2H), 7.36-7.33 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.03-7.01 (m, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.79, 147.93, 147.80, 137.91, 133.95, 130.24, 128.25, 123.57, 114.57, 55.40.

3-(4-(Trifluoromethoxy)phenyl)-pyridine (Scheme 3, 5e)[12]



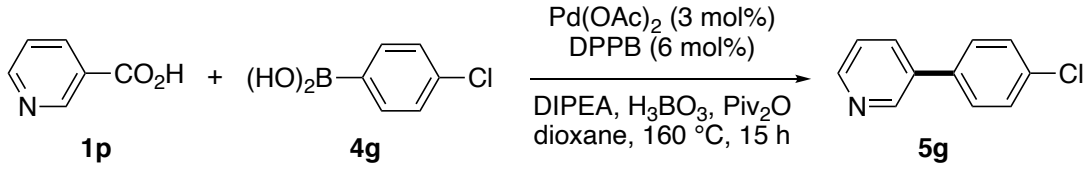
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-(trifluoromethyl)phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 81% yield (36.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 (s, 1H), 8.67 (s, 1H), 7.92-7.90 (d, *J* = 7.9 Hz, 1H), 7.76-7.69 (m, 4H), 7.44-7.41 (dd, *J* = 7.8, 4.8 Hz 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.36, 148.33, 141.39, 135.34, 134.58, 130.26 (q, J^F=32 Hz), 127.52, 126.07 (q, J^F=4.0 Hz), 124.10 (d, J^F=270 Hz),123.75. **^{19}F NMR (376MHz, $CDCl_3$)** δ -62.56.

4-(Pyridin-3-yl)benzonitrile (Scheme 3, 5f)[12]



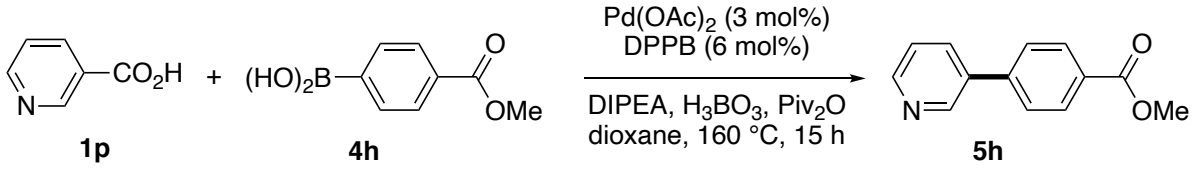
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-cyanophenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 94% yield (33.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.86 (s, 1H), 8.68 (s, 1H), 7.92-7.90 (d, *J* = 8.3 Hz, 1H), 7.80-7.78 (d, *J* = 8.5 Hz, 2H), 7.71-7.69 (d, *J* = 8.5 Hz, 2H), 7.46-7.43 (dd, *J* = 7.8, 4.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.61, 148.12, 142.26, 134.67, 132.92, 127.83, 123.93, 118.55, 116.46, 112.02.

3-(4-Chlorophenyl)pyridine (Scheme 3, 5g)[14]



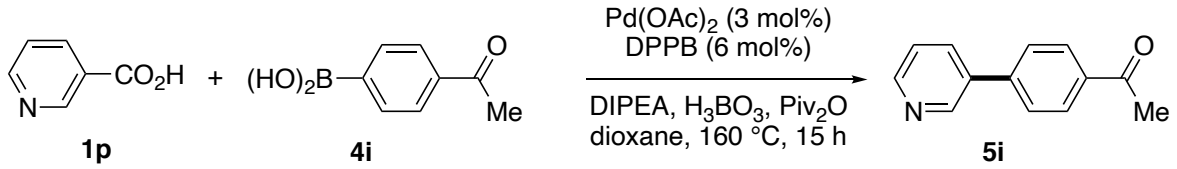
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2mmol, 1.0 equiv), 4-chlorophenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bisdiphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (23.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.83 (s, 1H), 8.62-8.60 (d, *J* = 5.9 Hz,1H), 7.86-7.84 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (d, *J* = 6.5 Hz, 2H), 7.47-7.44 (d, *J* = 8.6 Hz, 2H), 7.40-7.37 (dd, *J* = 7.8,4.8 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.66, 148.02, 136.25, 135.63, 134.37, 129.34, 128.43, 127.19, 123.71.

Methyl-4-(pyridin-3-yl)benzoate (Scheme 3, 5h)[12]



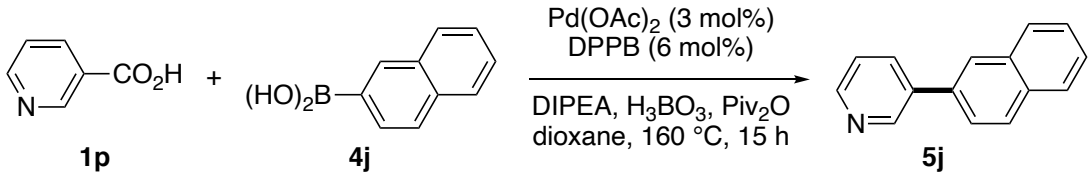
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (41.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (s, 1H), 8.65 (s,1H), 8.16-8.14 (d, *J* = 8.5 Hz, 2H), 7.93-7.91 (d, *J* = 9.5 Hz, 1H), 7.68-7.65 (d, *J* = 8.5, 2H), 7.43-7.40 (m, 1H), 3.95 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.04 149.34, 148.35, 142.37, 136.54, 135.50, 134.55, 130.11, 129.17, 127.33, 52.16.

1-(4-(Pyridin-3-yl)phenyl)ethanone (Scheme 3, 5i)[12]



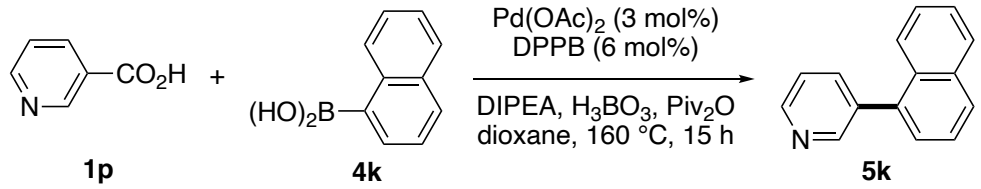
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 4-acetylphenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (37.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.89 (s, 1H), 8.65 -8.64 (d, *J* = 5.6 Hz, 1H), 8.09-8.07 (d, *J* = 8.5 Hz, 2H), 7.93-7.91 (d, *J* = 8.0 Hz, 1H), 7.70-7.68 (d, *J* = 8.0 Hz, 2H), 7.43-7.40 (dd, *J* = 7.7, 4.8 Hz, 1H), 2.66 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.60, 149.33, 148.34, 142.36, 136.54, 134.54, 129.16, 129.03, 127.47, 127.32, 26.74.

3-(Naphthalen-2-yl)pyridine (Scheme 3, 5j)[12]



According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 2-naphthaleneboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 93% yield (38.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.00 (s, 1H), 8.64 (s, 1H), 8.05 (s, 1H), 8.02-8.0 (d, *J* = 7.9 Hz, 1H), 7.98-7.88 (m, 4H), 7.73-7.71 (dd, *J* = 8.5, 1.8Hz, 1H), 7.75-7.52 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 148.53, 148.46, 135.13, 134.67, 133.59, 132.90, 132.25, 128.93, 128.26, 127.73, 126.65, 126.49, 126.20, 125.05, 123.70.

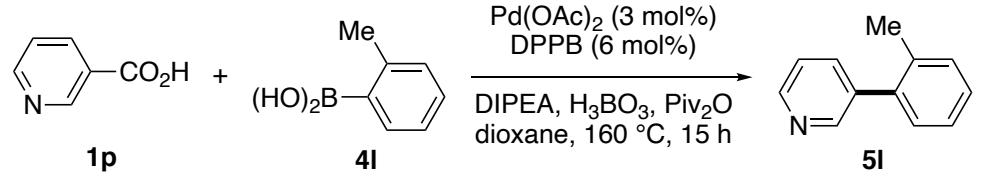
3-(Naphthalen-1-yl)pyridine (Scheme 3, 5k)[13]



1p **4k** **5k**

According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 1-naphthylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (25.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.78-8.71 (d, *J* = 28.4 Hz, 2H), 7.95-7.91 (t, *J* = 7.0 Hz, 2H), 7.85-7.80 (dd, *J* = 15.2, 8.1 Hz, 2H), 7.58-7.53 (m, 2H), 7.51-7.49 (dd, *J* = 8.6,1.4 Hz, 1H), 7.48-7.45 (m,1H), 7.44-7.42 (dd, *J* = 7.0,1.1 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 150.57, 148.40, 137.55, 136.26, 133.81, 131.47, 128.60, 128.51, 127.44, 126.60, 126.14, 125.42, 125.28, 124.33, 123.25.

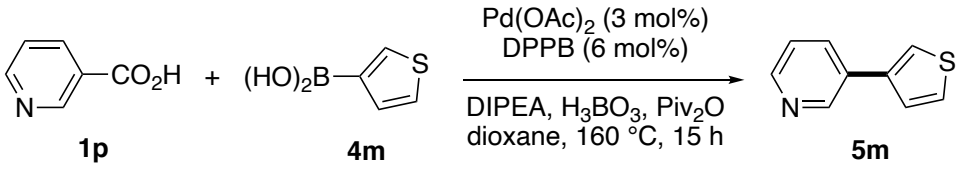
3-(o-Tolyl)pyridine (Scheme 3, 5l)[15]



1p **4l** **5l**

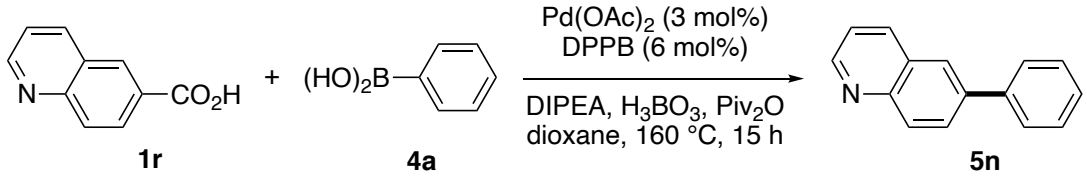
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 2-methylphenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 62% yield (21.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.94 (s, 1H), 8.81-8.79 (dd, *J* = 4.8,1.4 Hz, 1H), 8.16-8.13 (dt, *J* = 7.9,2.0 Hz, 1H), 7.68-7.65 (dt, *J* = 7.8,1.9 Hz, 3H), 7.46-7.42 (m, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.68, 147.84, 137.97, 136.74, 135.60, 131.12, 130.58, 129.87, 128.16, 126.10, 123.12, 20.38.

3-(Thiophen-3-yl)pyridine (Scheme 3, 5m)[12]



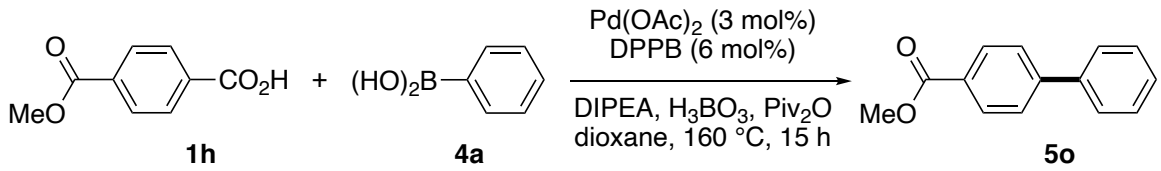
According to the general procedure, the reaction of 3-pyridinecarboxylic acid (0.2 mmol, 1.0 equiv), 3-thiopheneboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 80% yield (25.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.07 (s, 1H), 8.83 (s, 1H), 8.18-8.16 (d, *J* = 7.9 Hz, 1H), 7.98-7.97 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.62-7.61 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.50-7.46 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.45-7.43 (dd, *J* = 5.1, 2.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.62, 150.04, 140.71, 136.87, 134.65, 134.30, 128.29, 126.94, 123.62.

6-Phenylquinoline (Scheme 3, 5n)[12]



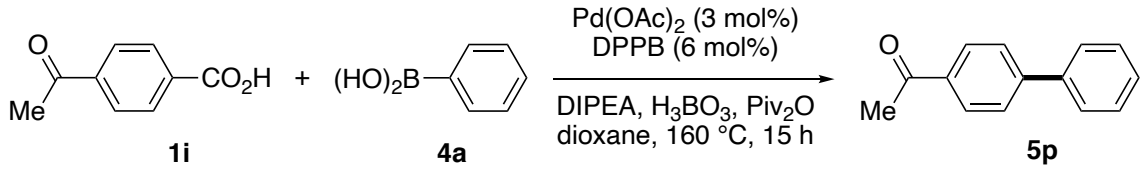
According to the general procedure, the reaction of quinoline-6-carboxylic acid (0.2 mmol, 1.0 equiv), phenyl boronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 76% yield (31.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.05-9.04 (d, *J* = 3.2 Hz, 1H), 8.31-8.25 (m, 3H), 8.20-8.17 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.87-7.85 (m, 2H), 7.67-7.63 (t, *J* = 7.4 Hz, 1H), 7.55-7.52 (t, *J* = 7.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.20, 137.88, 137.37, 135.66, 132.80, 131.37, 130.14, 129.82, 129.56, 128.52, 1276.36, 126.15, 122.03.

Methyl-[1,1'-biphenyl]-4-carboxylate (Scheme 4, 5o)[12]



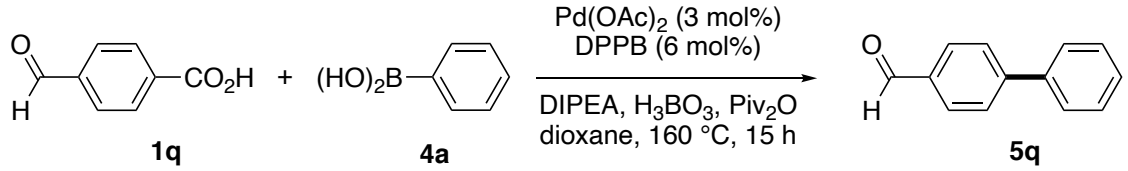
According to the general procedure, the reaction of 4-(methoxycarbonyl) benzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (34.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.13-8.10 (d, *J* = 10.4 Hz, 2H), 7.68-7.62 (dd, *J* = 15.2, 8.3 Hz, 4H), 7.49-7.45 (t, *J* = 7.4 Hz, 2H), 7.40-7.38 (d, *J* = 8.5 Hz, 1H), 3.95 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.04, 145.65, 140.02, 130.11, 128.94,128.89, 128.16, 127.30, 127.07, 51.16.

1-([1,1'-Biphenyl]-4-yl)ethanone (Scheme 4, 5p)[12]



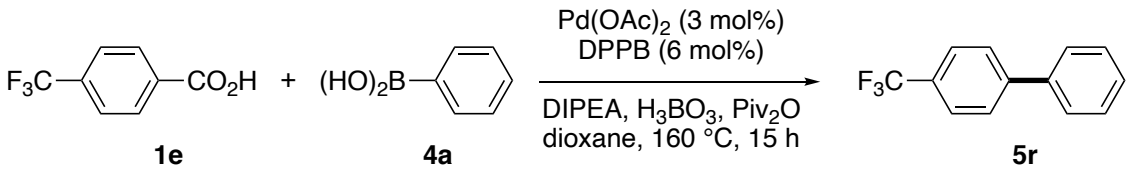
According to the general procedure, the reaction of 4-acetylbenzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 75% yield (22.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05-8.03 (d, *J* = 8.5 Hz, 2H), 7.70-7.69 (d, *J* = 6.7 Hz, 2H), 7.65-7.63 (d, *J* = 8.5 Hz, 2H), 7.50-7.46 (t, *J* = 7.9 Hz, 2H), 7.42-7.39 (t, J=7.3 Hz 1H), 2.65 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 197.82, 145.81, 139.89, 135.85, 128.97, 128.94, 128.25, 127.29, 127.25, 26.70.

[1,1'-Biphenyl]-4-carbaldehyde (Scheme 4, 5q)[12]



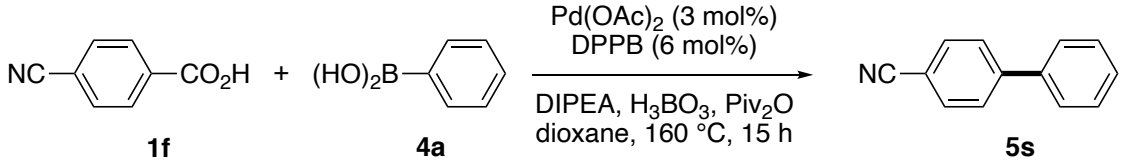
According to the general procedure, the reaction of 4-formylbenzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (33.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 7.97-7.95 (d, *J* = 8.4 Hz, 2H), 7.77-7.75 (d, *J* = 8.2 Hz, 2H), 7.66-7.63 (m, 2H), 7.51-7.47 (td, *J* = 6.6, 6.1, 1.5 Hz, 2H), 7.44-7.40 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.99, 147.22 139.72, 135.17, 130.29, 129.03, 128.49, 127.70, 127.38.

4-(Trifluoromethyl)-1,1'-biphenyl (Scheme 4, 5r)[12]



According to the general procedure, the reaction of 4-(trifluoromethyl) benzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (42.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (s, 4H), 7.62-7.60 (d, *J* = 7.2 Hz, 2H), 7.50-7.47 (t, *J* = 7.1 Hz, 2H), 7.43-7.41 (d, *J* = 7.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 144.74, 139.78, 129.33 (q, J^F= 32 Hz), 129.00, 128.19, 127.43, 127.29, 125.72 (q, J^F= 3 Hz), 124.31 (q, J^F= 270 Hz). **^{19}F NMR (376 MHz, CDCl3)** δ -62.37.

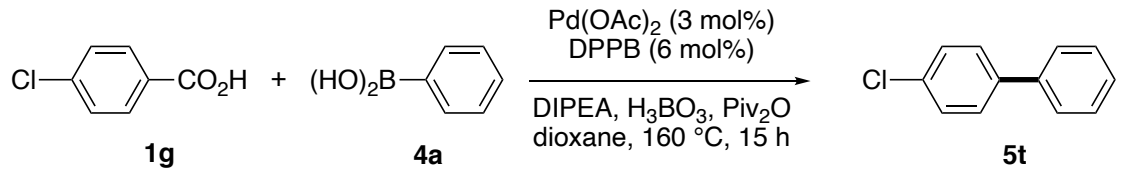
[1,1'-Biphenyl]-4-carbonitrile (Scheme 4, 5s)[12]



1f **4a** **5s**

According to the general procedure, the reaction of 4-cyanobenzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (22.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74-7.68 (m, 4H), 7.61-7.58 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.51-7.47 (m, 2H), 7.45-7.43 (d, *J* = 8.6, Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.70, 139.19, 132.62, 129.13, 128.67, 127.75, 127.25, 118.97, 110.92.

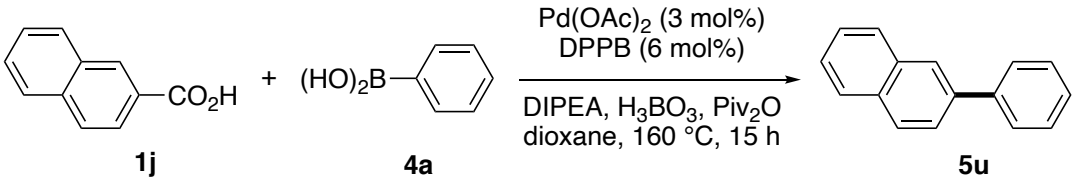
4-Chloro-1,1'-biphenyl (Scheme 4, 5t)[17]



1g **4a** **5t**

According to the general procedure, the reaction of 4-chlorobenzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 60% yield (24.1 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82-7.75 (m, 4H), 7.63-7.59 (t, *J* = 8.0 Hz, 1H), 7.51-7.46 (dd, *J* = 8.0, 4.0 Hz, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.93, 137.26, 135.88, 132.68, 131.50, 129.96, 128.67, 128.43.

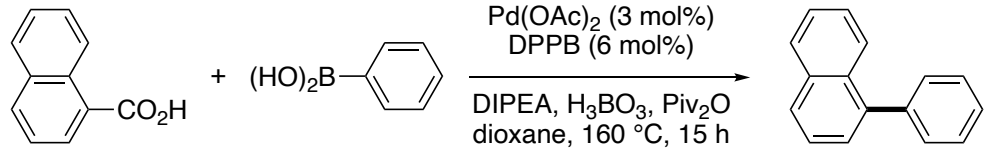
2-Phenylnaphthalene (Scheme 4, 5u)[18]



1j **4a** **5u**

According to the general procedure, the reaction of 2-naphthalenecarboxylic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenyl-phosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 54% yield (22.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (s, 1H), 7.93-7.86 (m, 3H), 7.77-7.72 (m, 3H), 7.52-7.47 (m, 4H), 7.40-7.37 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.57, 133.68, 132.62, 128.87, 128.43, 128.21, 127.66, 127.45, 127.37, 126.30, 125.95, 125.82, 125.61

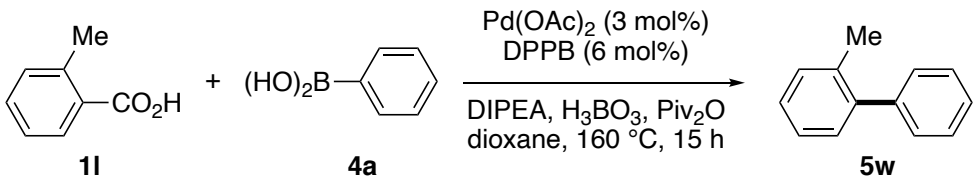
1-Phenylnaphthalene (Scheme 4, 5v)[12]



1k **4a** **5v**

According to the general procedure, the reaction of 1-naphthoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenyl-phosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 74% yield (30.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93-7.91 (d, *J* = 8.4 Hz, 2H), 7.89-7.86 (d, *J* = 8.2 Hz, 1H), 7.56-7.47 (m, 6H), 7.46-7.42 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 140.75, 140.26, 133.78, 131.61, 130.08, 128.27, 127.63, 127.24, 126.93, 126.03, 125.77, 125.39.

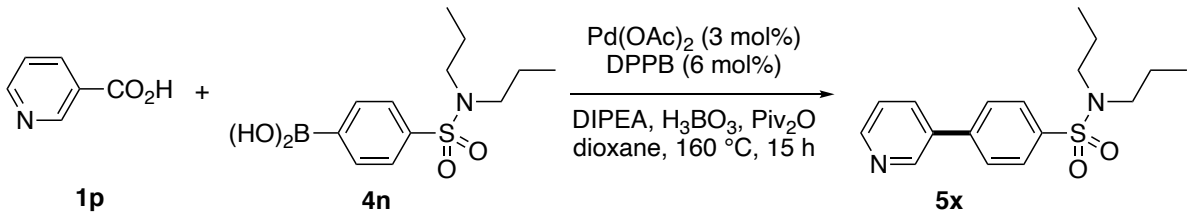
2-Methyl-1,1'-biphenyl (Scheme 4, 5w)[17]



1l **4a** **5w**

According to the general procedure, the reaction of 2-methylbenzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenyl-phosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 57% yield (19.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.40 (t, *J* = 7.2 Hz, 2H), 7.36-7.32 (m, 3H), 7.27-7.26 (d, *J* = 3.6 Hz, 2H), 7.25-7.23 (m, 2H), 2.28 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 141.95, 135.82, 135.36, 129.80, 129.28, 129.20, 128.07, 127.25, 127.15, 126.76, 125.76, 125.53, 20.48.

***N,N*-dipropyl-4-(pyridin-3-yl)benzenesulfonamide (Scheme 5, 5x)**

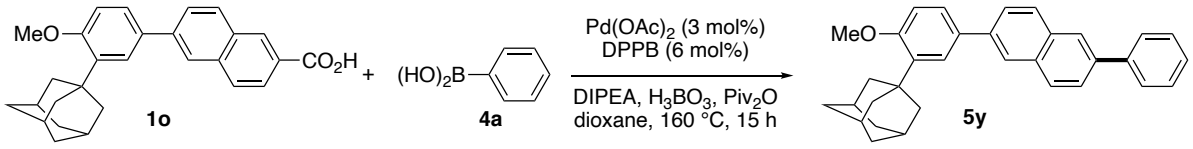


1p **4n** **5x**

According to the general procedure, the reaction of probenecid (0.2 mmol, 1.0 equiv), 3-pyridine-carboxylic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 67% yield (39.4 mg). *New compound*. Yellow solid. **Mp** = 82-84℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 (s, 1H), 8.66-8.65 (d, *J* = 4.0 Hz, 1H), 7.92-7.90 (d, *J* = 8.0 Hz, 3H), 7.71-7.69(d, *J* = 8.0 Hz, 2H), 7.45-7.42 (q, *J* = 4.0 Hz, 1H), 3.13-3.09 (t, *J* = 8.0 Hz, 4H), 1.63-1.53 (m, 4H), 0.90-0.87 (t, *J* = 4.0 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.24, 148.08, 141.54, 139.83, 135.16, 134.81, 127.85, 127.67, 123.88, 50.09, 22.08, 11.21. **HRMS-ESI** calcd for

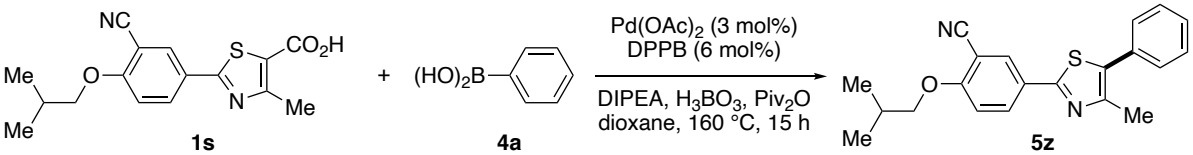
(M^++H) 319.1480. found 319.1482. **IR:** 2965.21, 2875.26, 1667.88, 1586.15, 1467.68, 1425.02, 1153.69, 798.74.

(3r,5r,7r)-1-(2-Methoxy-5-(6-phenylnaphthalen-2-yl)-phenyl)adamantane (Scheme 5, 5y)



According to the general procedure, the reaction of adapalene (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenyl-phosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 76% yield (67.5 mg). *New compound*. Yellow solid. **Mp** = 78-80 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 8.05 (s, 1H), 7.98-7.95 (d, *J* = 11.8 Hz, 3H), 7.89-7.86 (m, 2H), 7.83-7.80 (d, *J* = 8.6 Hz, 1H), 7.63-7.61 (d, *J* = 2.9 Hz, 2H), 7.58-7.51 (q, *J* = 8.0, 7.3 Hz, 3H), 7.02-7.00 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.98, 141.53, 139.06, 134.36, 132.30, 131.83,130.99, 130.09, 129.81, 128.40, 128.35, 126.62, 126.17, 125.99, 125.76, 124.78, 112.14, 55.20, 40.62, 37.14, 31.51, 29.12. **HRMS-ESI** calcd for (M^++H) 445.2526, found 445.2382. **IR:** 2902.81, 2850.75, 1625.64, 1462.27, 1060.54, 755.99, 691.72.

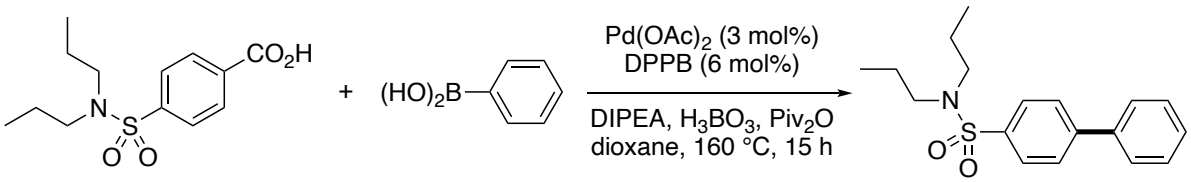
2-Isobutoxy-5-(4-methyl-5-phenylthiazol-2-yl)-benzonitrile (Scheme 5, 5z)



According to the general procedure, the reaction of febuxostat (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (57.1 mg). *New compound*. Yellow solid.

Mp = 62-64 °C. **^{1}H NMR (400 MHz, $CHCl_3$)** δ 8.13-8.12 (d, *J* = 2.2 Hz, 1H), 8.08-8.05 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.82-7.79 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.59-7.57 (d, *J* = 8.7 Hz, 1H), 7.50-7.44 (m, 2H),7.00- 6.98 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 0.9 Hz, 1H), 3.89-3.87 (d, *J* = 6.5 Hz, 2H), 2.49 (s, 3H), 2.23-2.16 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.09-1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.99, 161.70, 154.04, 137.59, 132.45, 132.15, 131.66, 130.09, 128.29, 126.93, 115.73, 113.52, 112.50, 102.67, 75.55, 27.11, 19.09, 17.21. **HRMS-ESI** calcd for (M^++H) 349.1375; found 349.1376. **IR:** 2923.88, 2853.09, 2227.89, 1730.90, 1659.22, 1505.13, 1446.94, 1012.71, 734.14, 702.16.

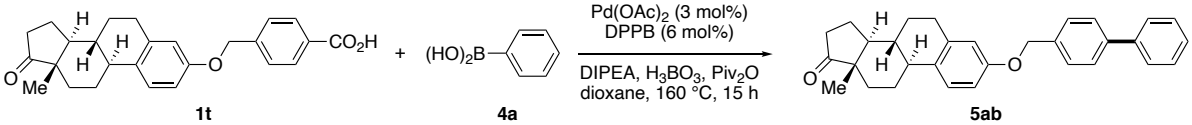
N,N-dipropyl-[1,1'-biphenyl]-4-sulfonamide(Scheme 5, 5aa)[12]



1n **4a** **5aa**

According to the general procedure, the reaction of probenecid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (61.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92-7.86 (m, 2H), 7.77-7.69 (d, *J* = 8.9 Hz, 2H), 7.62-7.60 (d, *J* = 7.9 Hz, 2H), 7.53-7.46 (m, 2H), 7.43-7.39 (dd, *J* = 8.2, 6.4 Hz, 1H), 3.13-3.09 (m, 4H), 1.61-1.55 (q, *J* = 7.5 Hz, 4H), 0.91-0.87 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.08, 139.40, 138.74, 130.12 129.03, 128.39, 127.58, 127.29, 50.12, 22.11, 11.23.

(13S)-3-([1,1'-Biphenyl]-4-ylmethoxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (Scheme 5, 5ab)



1t **4a** **5ab**

According to the general procedure, the reaction of 4-((((13S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)benzoic acid (0.2 mmol, 1.0 equiv), phenylboronic acid (2.0 equiv), $Pd(OAc)_2$ (3 mol%), 1,4-bis(diphenylphosphino)butane (6 mol%), *N,N*-diisopropylethylamine (2.0 equiv), H_3BO_3 (2.0 equiv) and trimethylacetic anhydride (2.0 equiv) in 1,4-dioxane (1.0 mL) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 63% yield (55.0 mg). *New compound*. Yellow solid. **Mp** = 56-58℃. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.84-7.79 (m, 4H), 7.62-7.58 (t, *J* = 8.0 Hz, 1H), 7.56-7.53 (d, *J* = 12.0 Hz, 2H), 7.51-7.47 (t, *J* =8.0 Hz, 2H), 7.23-7.21 (d, *J* = 8.0 Hz, 1H), 6.81-6.78 (dd, *J* = 8.0,4.0 Hz, 1H), 6.74 (s, 1H), 5.14 (s, 2H), 2.92-2.89 (q, *J* = 4.0 Hz, 3H), 2.54-2.47 (dd, *J* = 20.0, 8.0Hz, 1H), 2.41-2.39 (d, *J* = 8.0Hz, 1H), 2.29-1.94 (m, 8H), 1.68-1.60 (m, 2H), 1.51-1.49 (d, *J* = 8.0 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 195.92, 156.86, 148.55, 138.05, 137.43, 132.38, 130.17, 128.81, 128.57, 127.96, 127.37, 127.14, 121.62, 114.90, 112.40, 69.72, 50.41, 44.15, 37.98, 35.87, 31.54, 29.41, 26.34, 25.74, 21.60, 13.83. **HRMS-ESI** calcd for (M^++H) 437.2481; found 437.2473. **IR:** 2921.46, 2852.29, 1736.82, 1659.39, 1494.39, 1204.79, 799.06, 731.04, 704.61.

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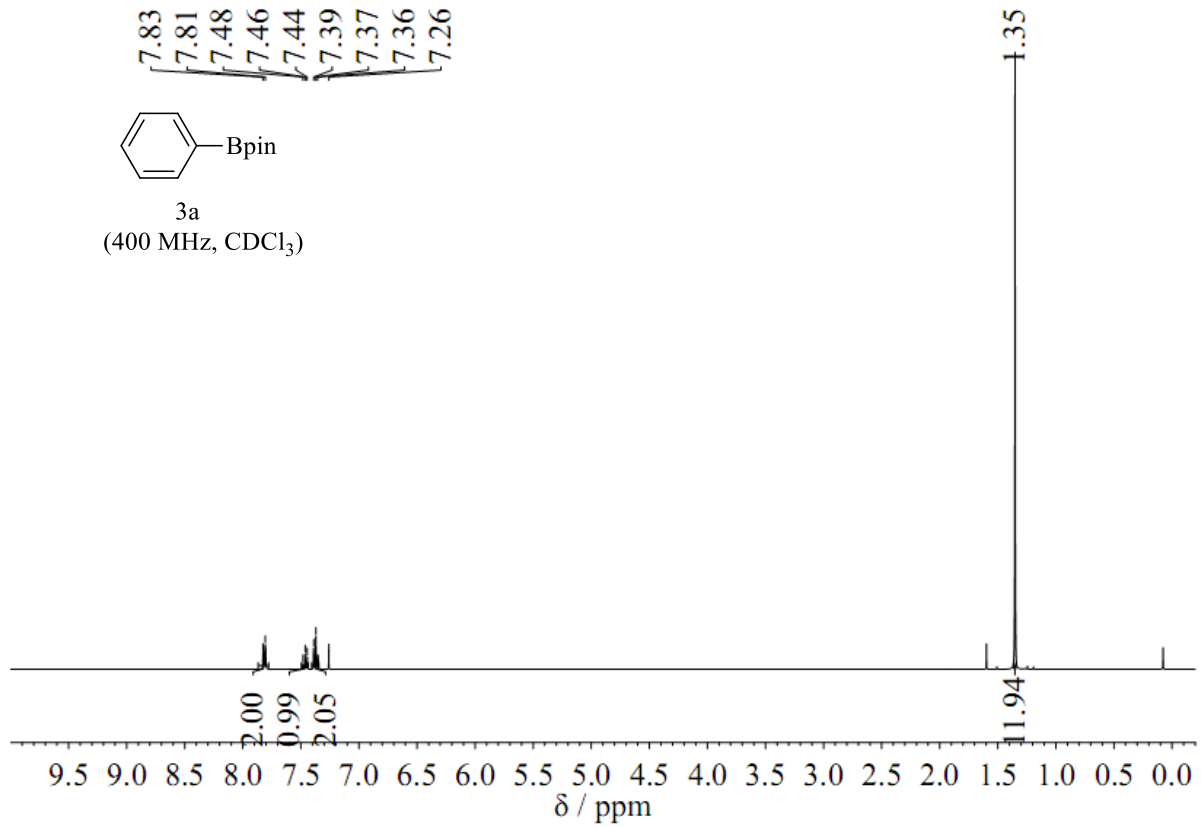
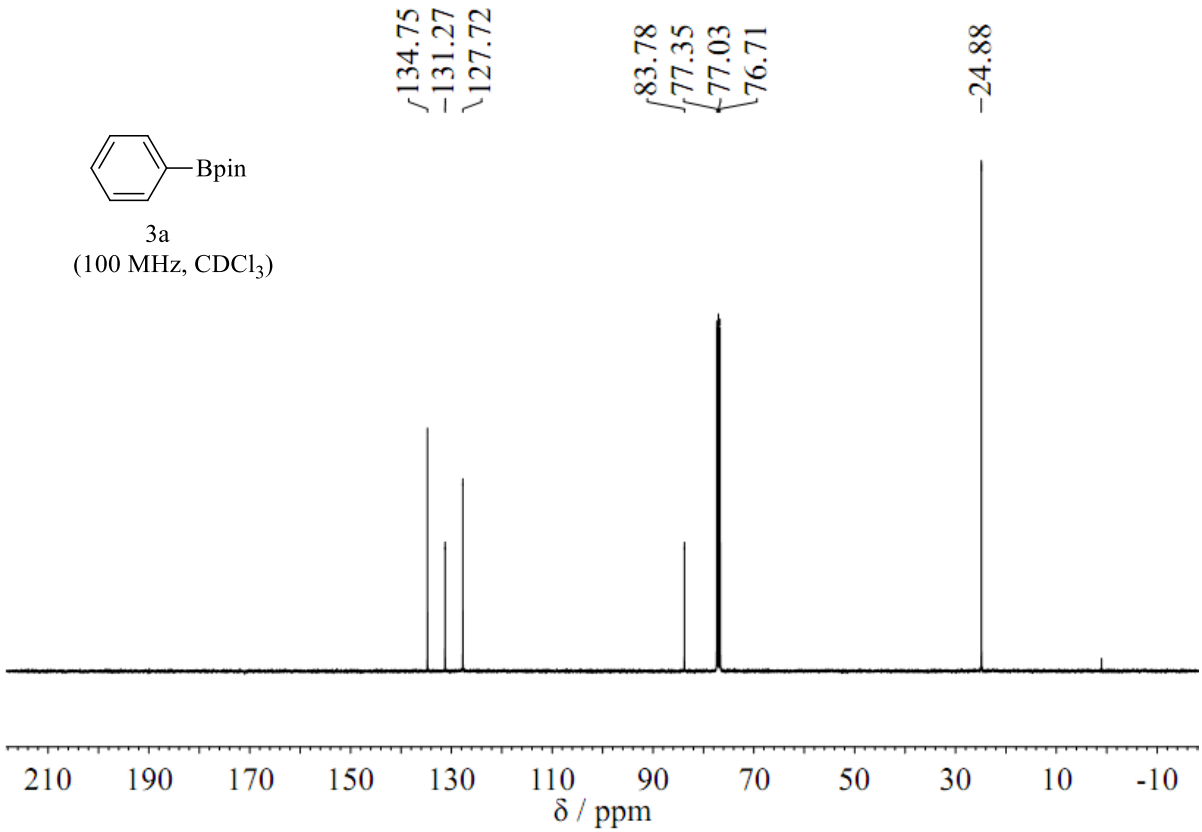
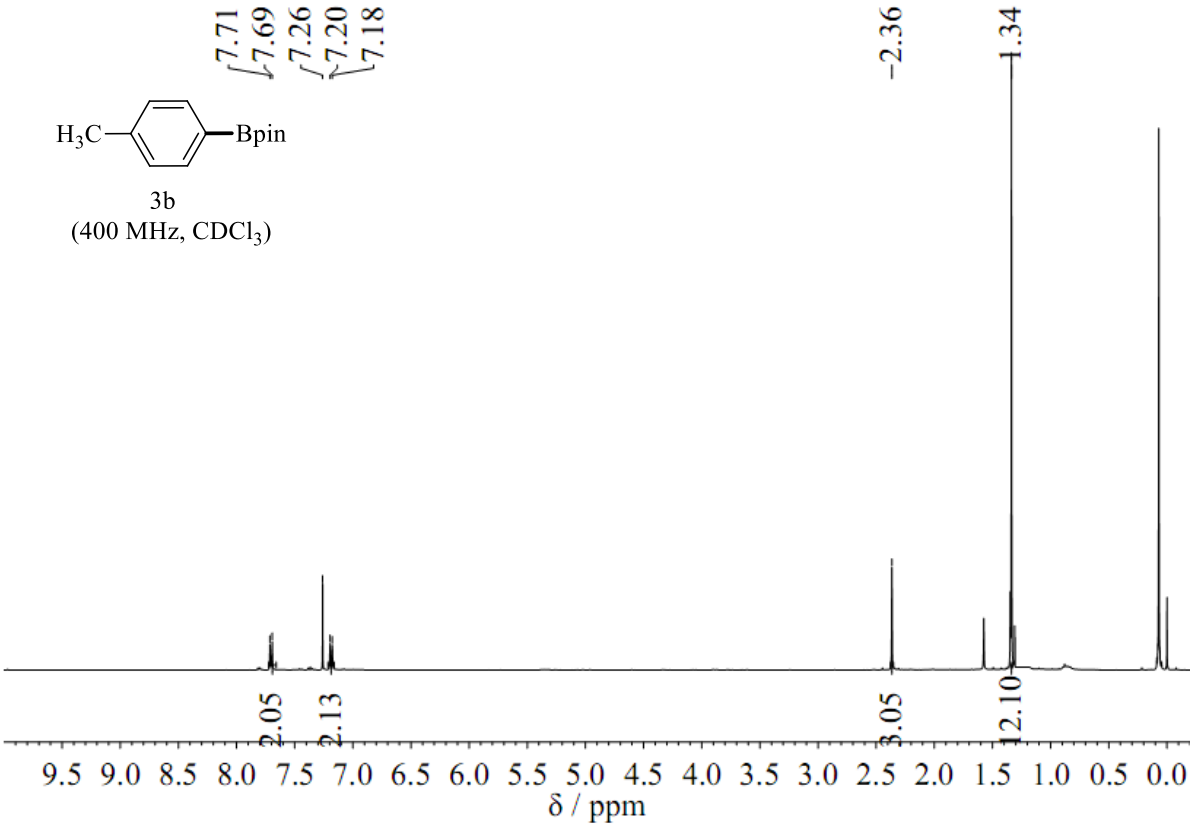
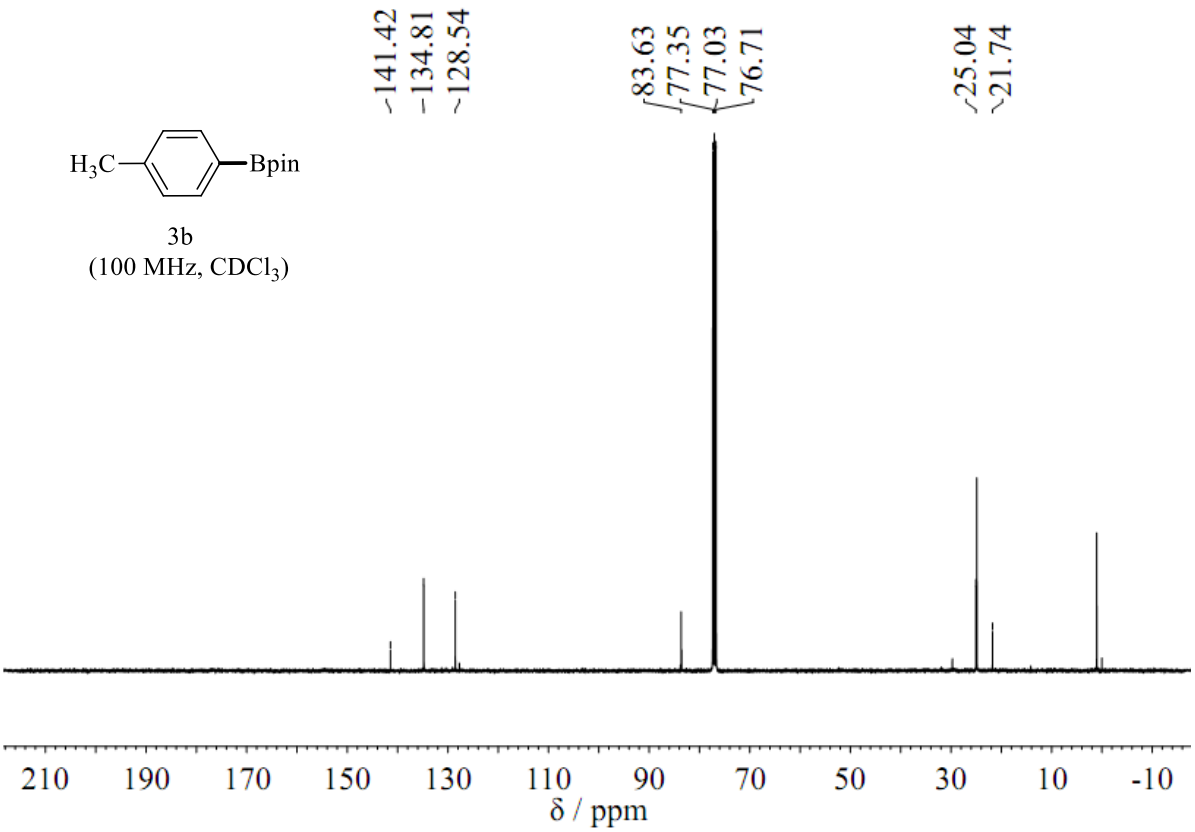
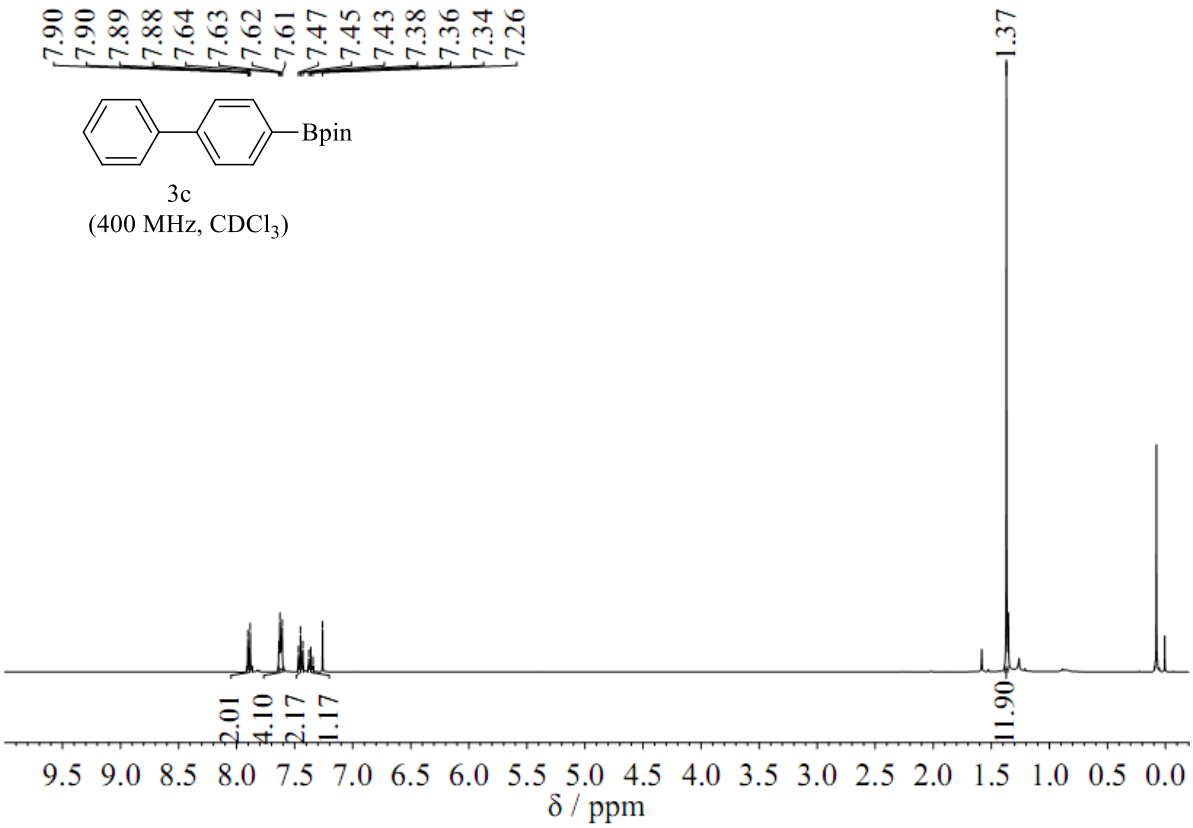
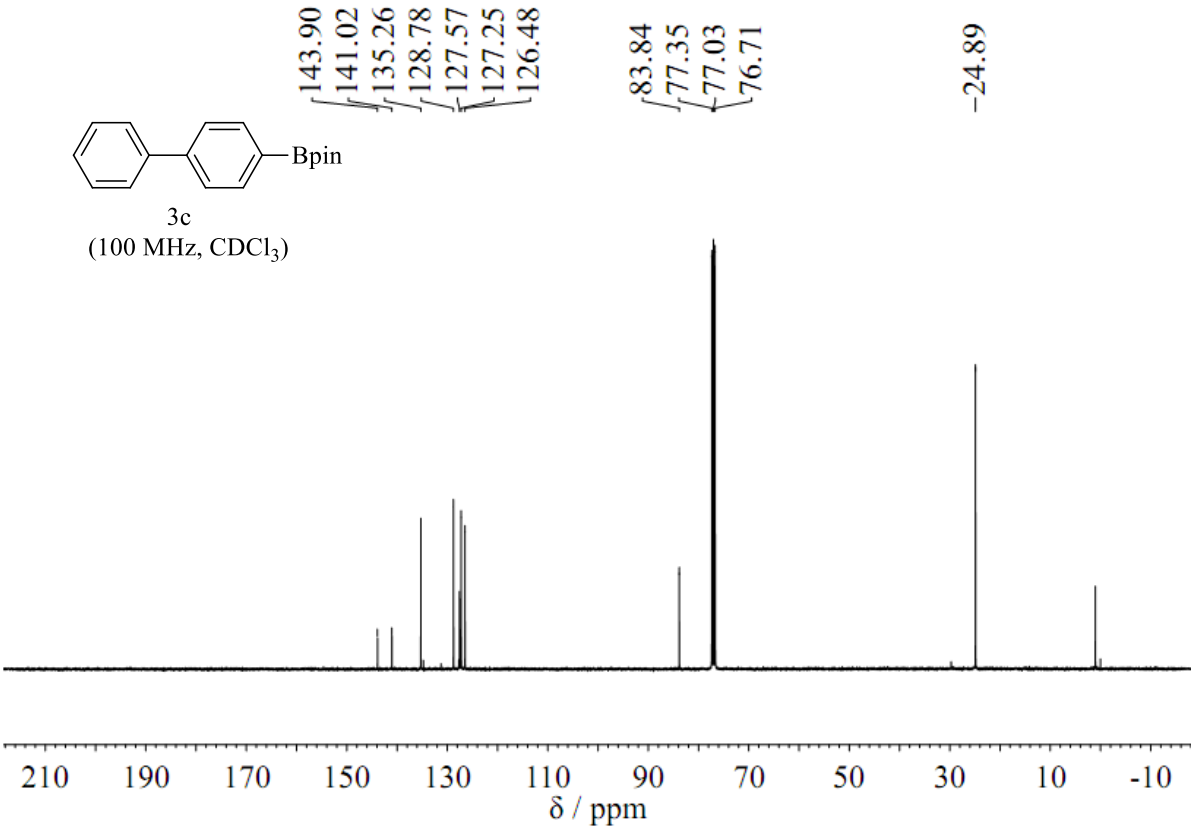

7.83
7.81
7.48
7.46
7.44
7.39
7.37
7.36
7.26
1.35
Bpin
3a
(400 MHz, CDCl3)
2.00
0.99
2.05
11.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

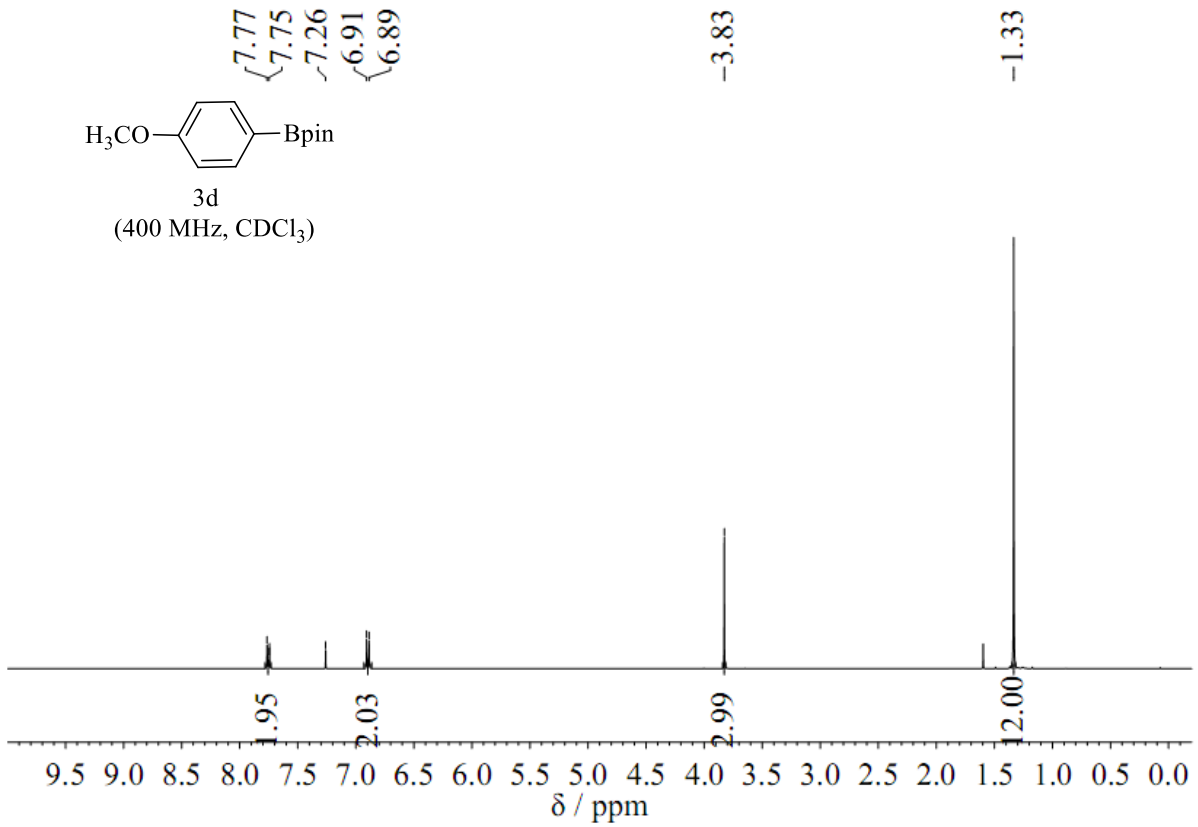

134.75
131.27
127.72
83.78
77.35
77.03
76.71
24.88
Bpin
3a
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

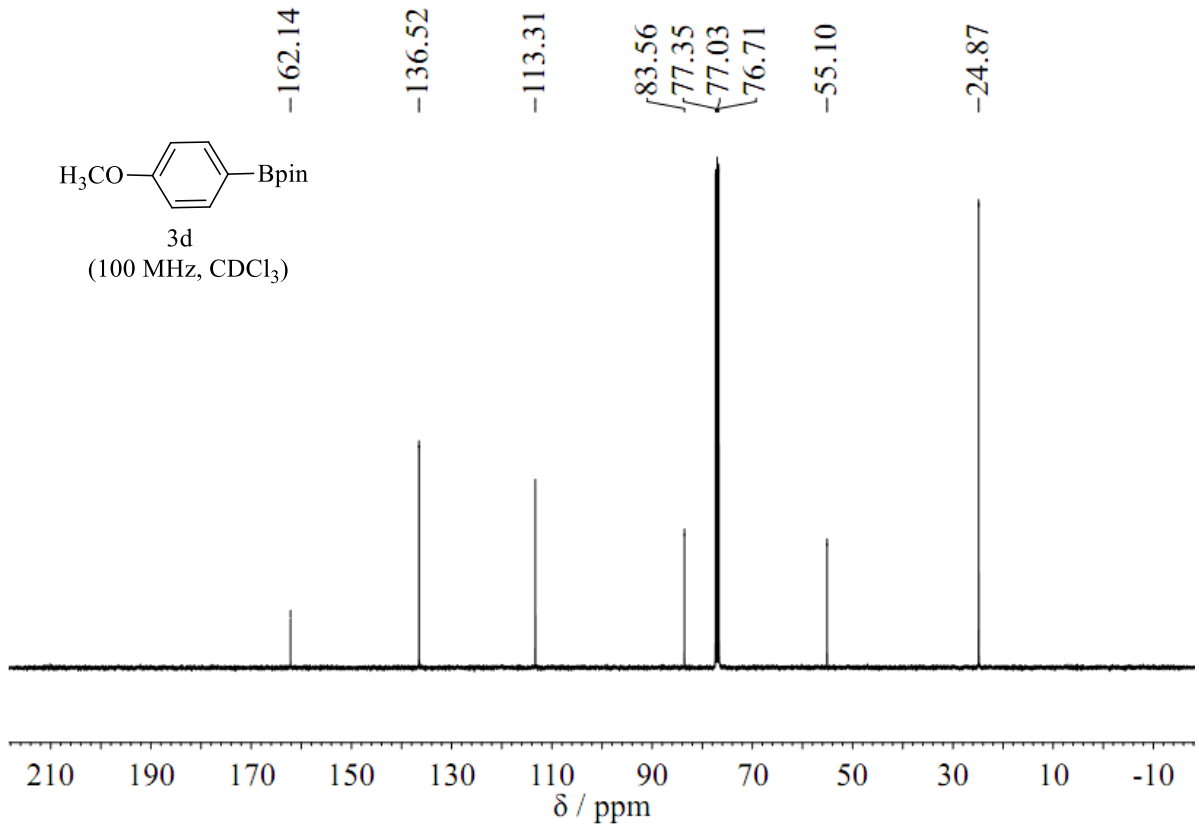

7.71
7.69
7.26
7.20
7.18
2.36
1.34
H3C
Bpin
3b
(400 MHz, CDCl3)
2.05
2.13
3.05
12.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

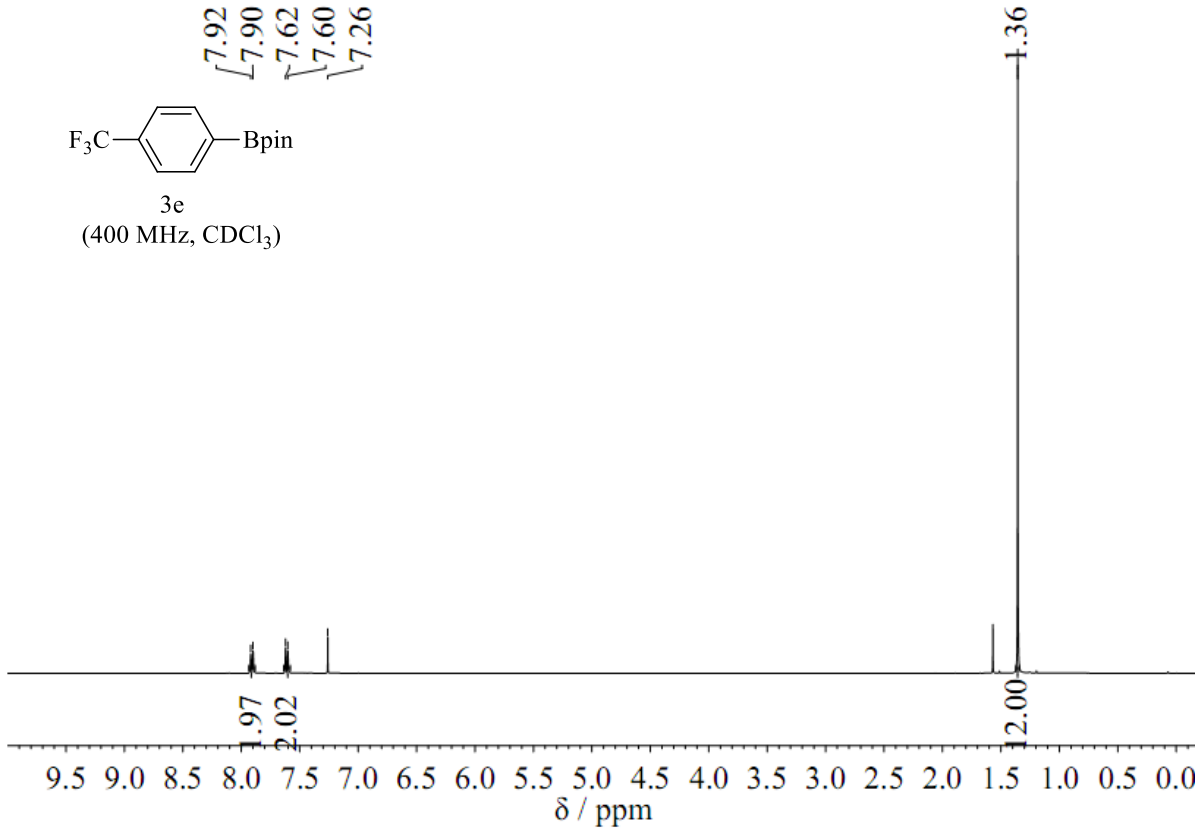

141.42
134.81
128.54
83.63
77.35
77.03
76.71
25.04
21.74
H3C
Bpin
3b
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

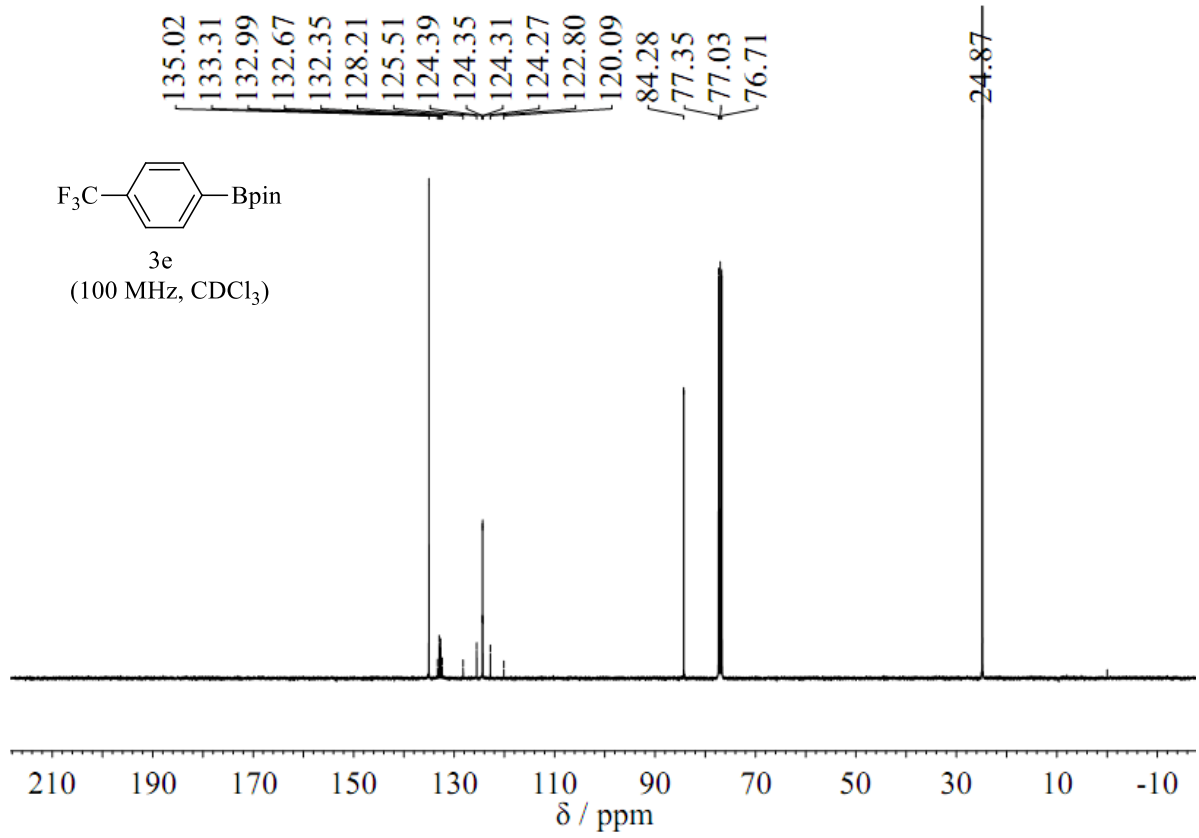

7.90
7.90
7.89
7.88
7.64
7.63
7.62
7.61
7.47
7.45
7.43
7.38
7.36
7.34
7.26
1.37
Bpin
3c
(400 MHz, CDCl3)
2.01
4.10
2.17
1.17
11.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

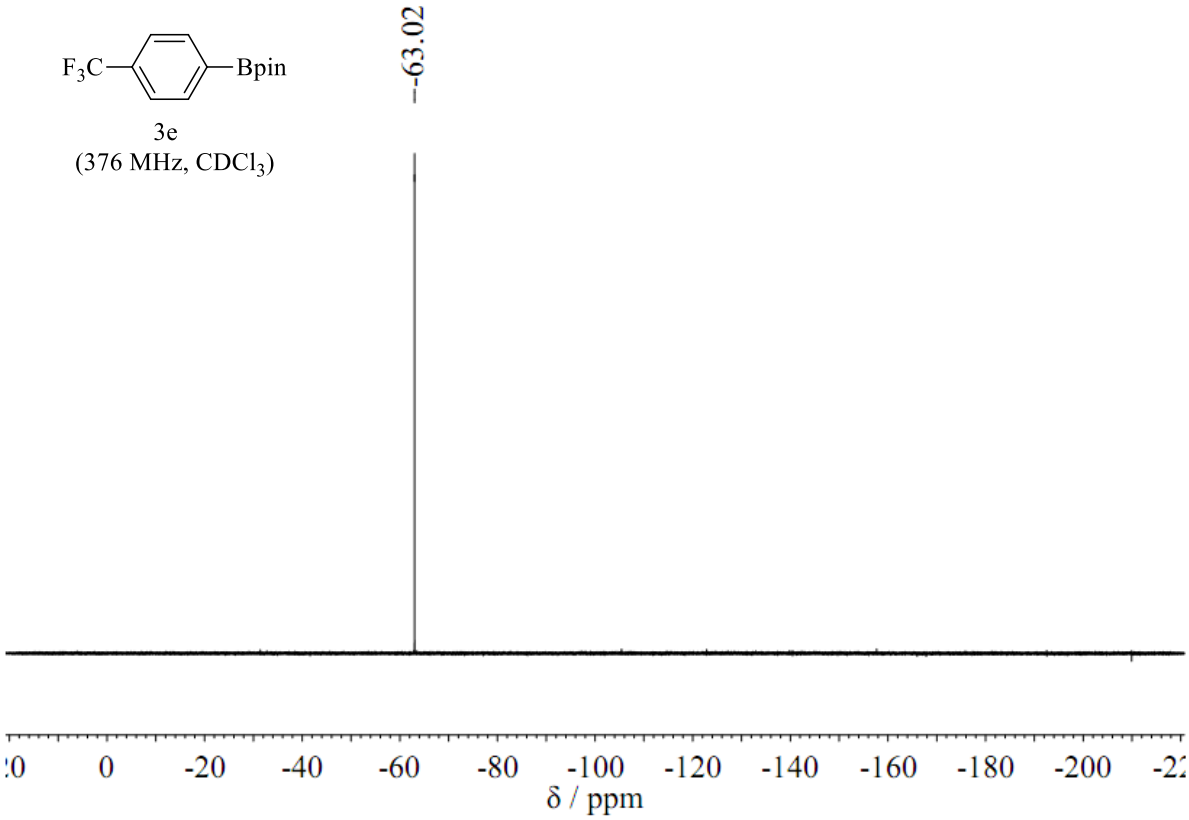

143.90
141.02
135.26
128.78
127.57
127.25
126.48
83.84
77.35
77.03
76.71
24.89
Bpin
3c
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

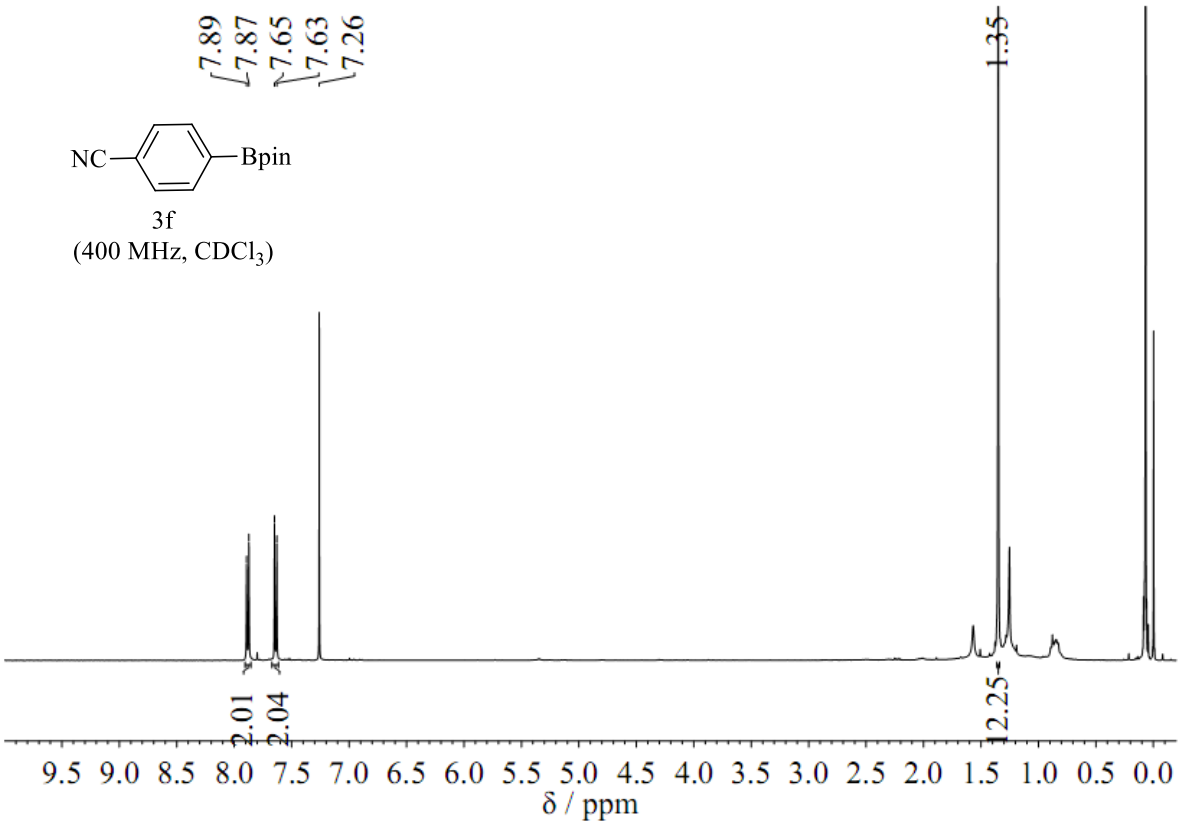

7.77
7.75
7.26
6.91
6.89
3.83
1.33
H3CO
Bpin
3d
(400 MHz, CDCl3)
1.95
2.03
2.99
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

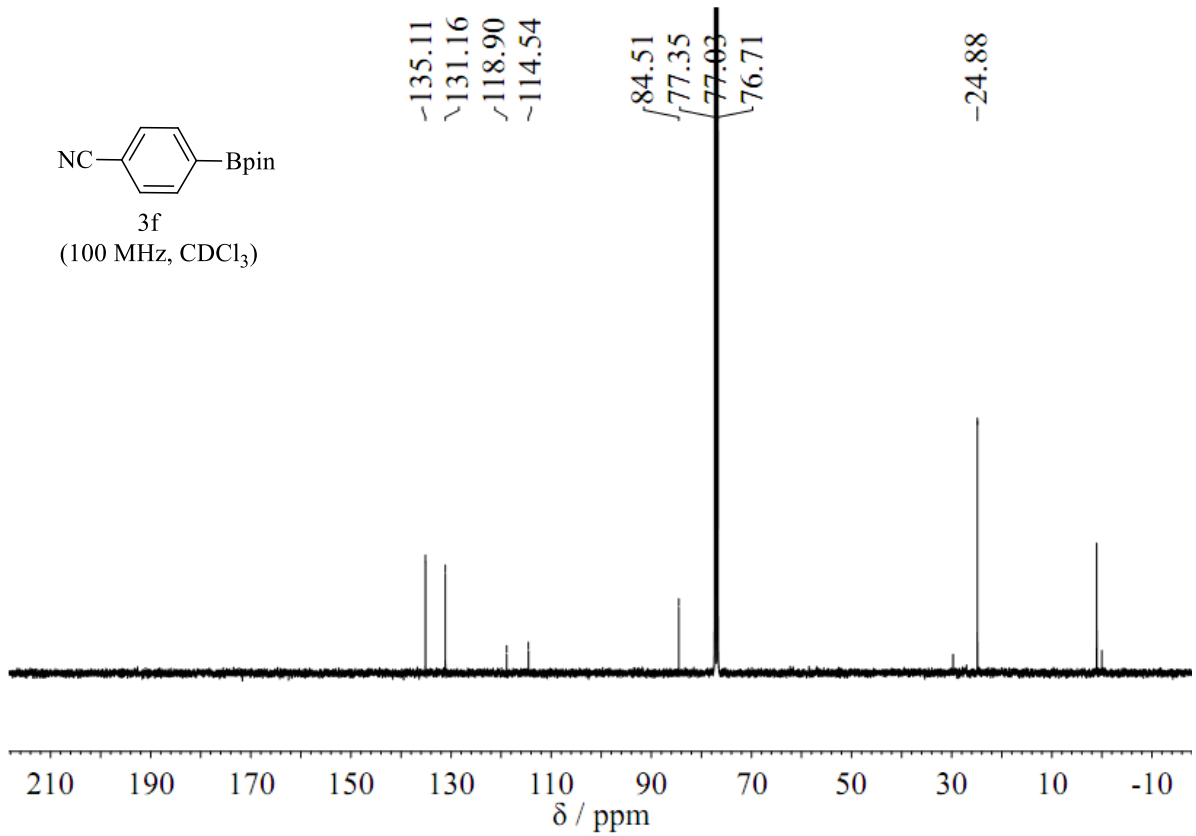

162.14
136.52
113.31
83.56
77.35
77.03
76.71
55.10
24.87
H3CO
Bpin
3d
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

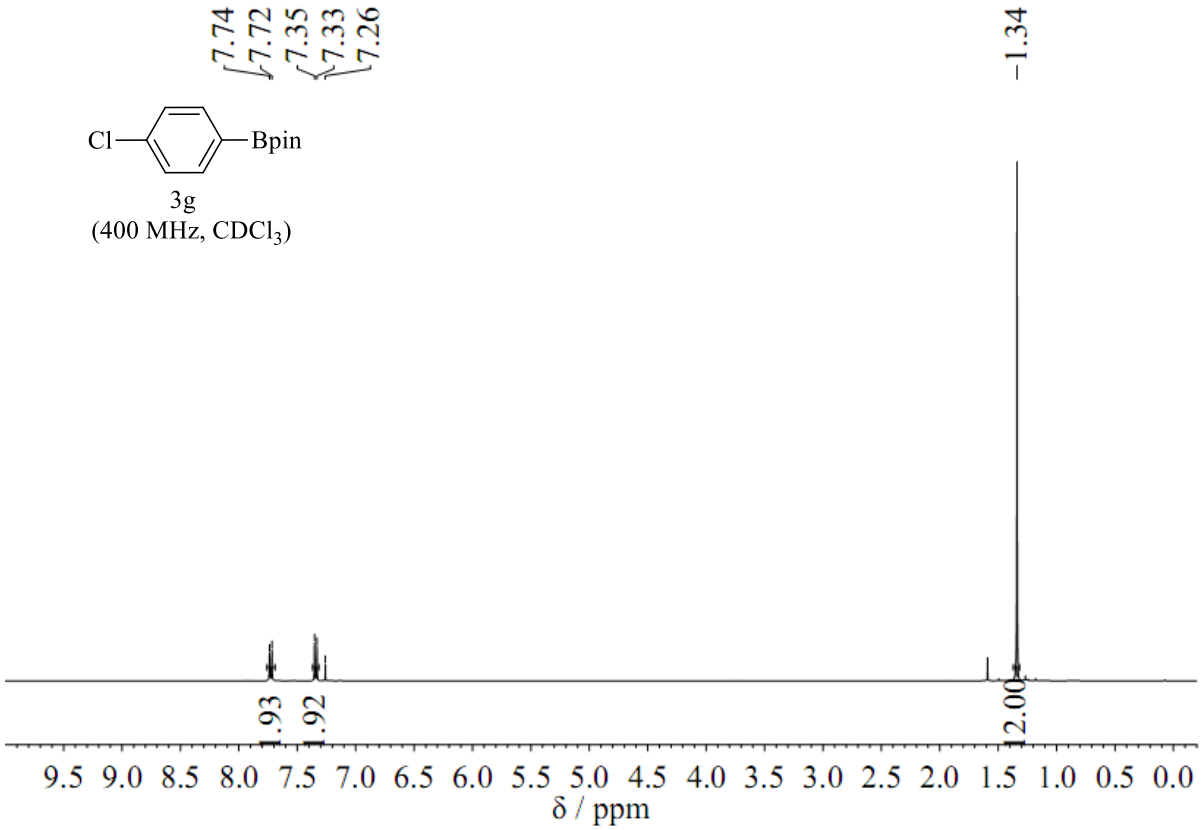

7.92
7.90
7.62
7.60
7.26
1.36
F3C
Bpin
3e
(400 MHz, CDCl3)
1.97
2.02
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

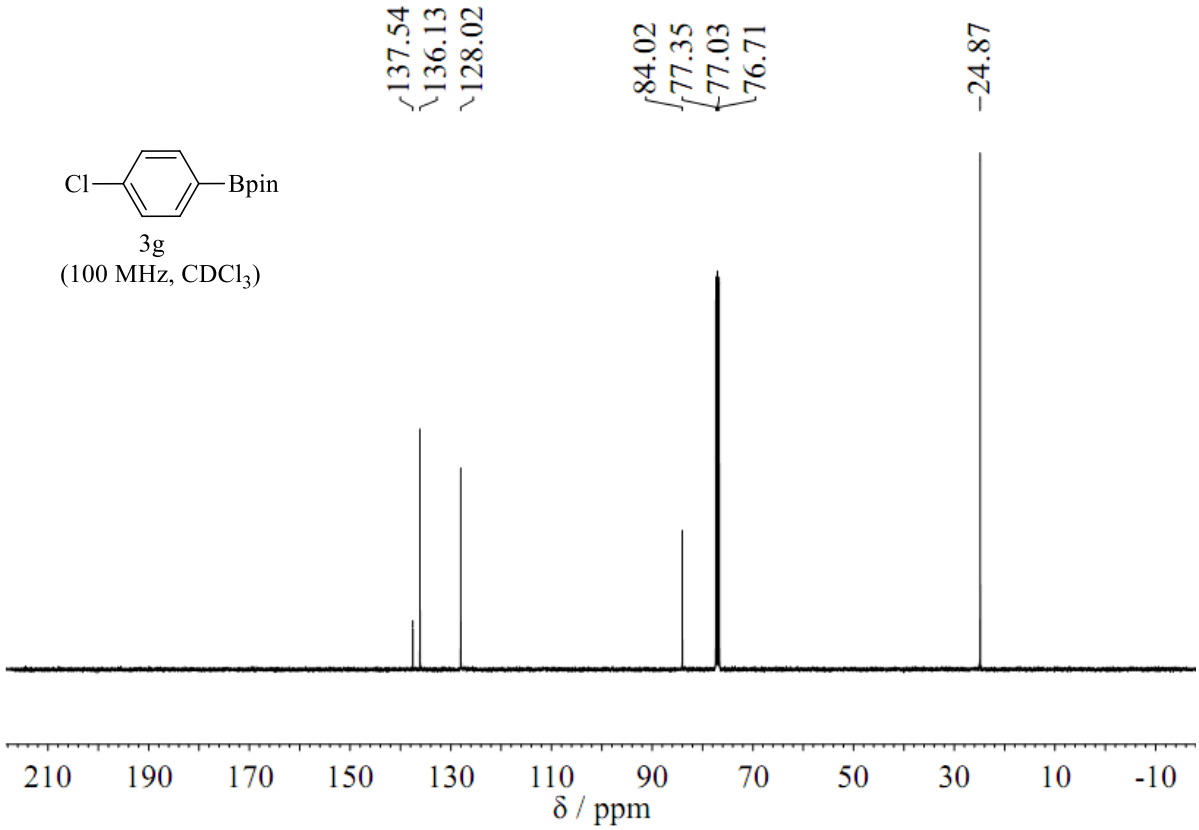

135.02
133.31
132.99
132.67
132.35
128.21
125.51
124.39
124.35
124.31
124.27
122.80
120.09
84.28
77.35
77.03
76.71
24.87
F3C
Bpin
3e
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

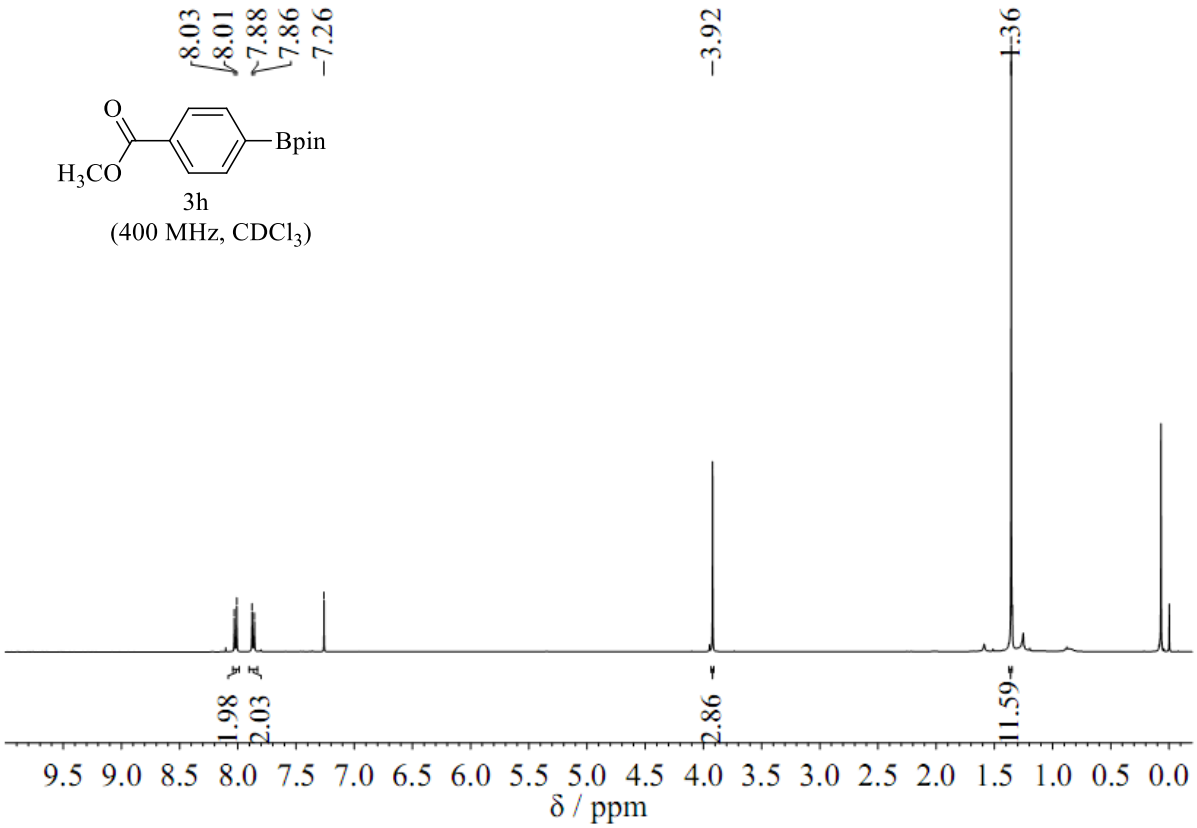

F3C
Bpin
3e
(376 MHz, CDCl3)
-63.02
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
δ / ppm


7.89
7.87
7.65
7.63
7.26
1.35
NC
Bpin
3f
(400 MHz, CDCl3)
2.01
2.04
12.25
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
δ / ppm

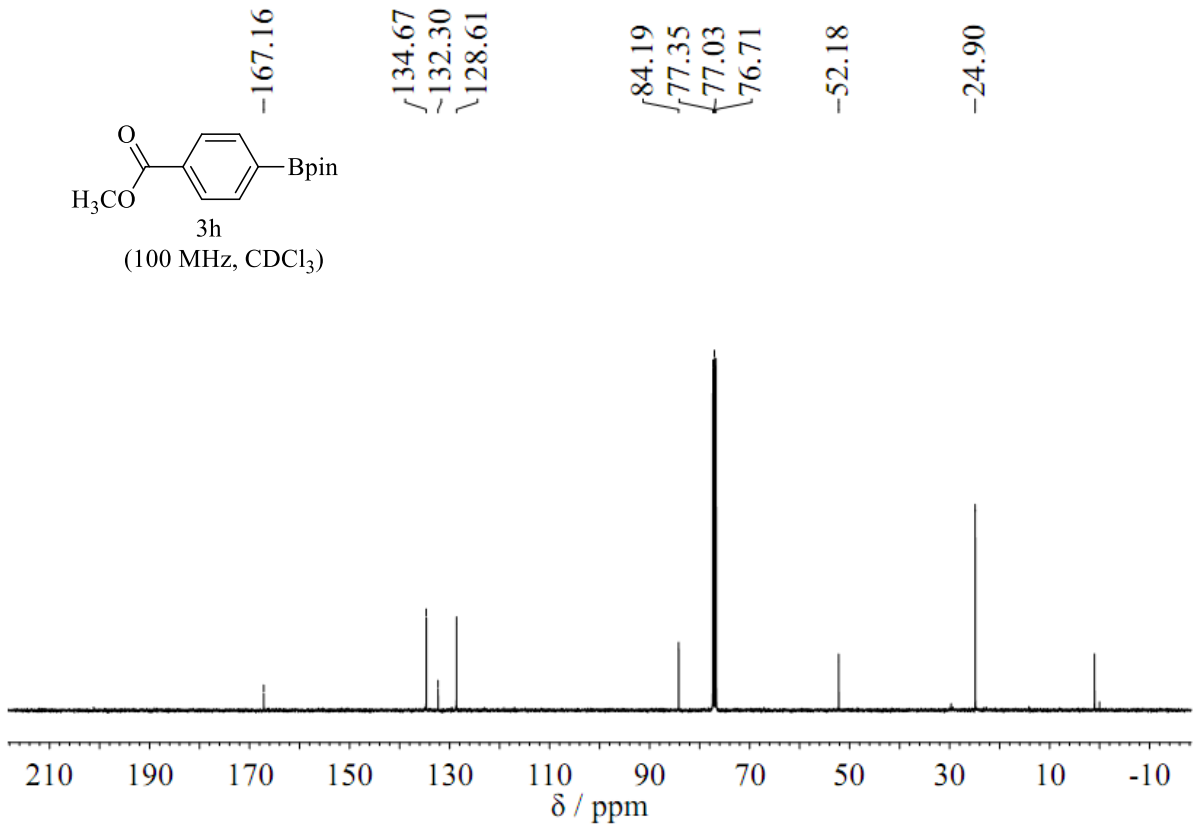

135.11
131.16
118.90
114.54
84.51
77.35
77.03
76.71
24.88
NC
Bpin
3f
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


7.74
7.72
7.35
7.33
7.26
1.34
Cl
Bpin
3g
(400 MHz, CDCl3)
1.93
1.92
2.00
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
δ / ppm

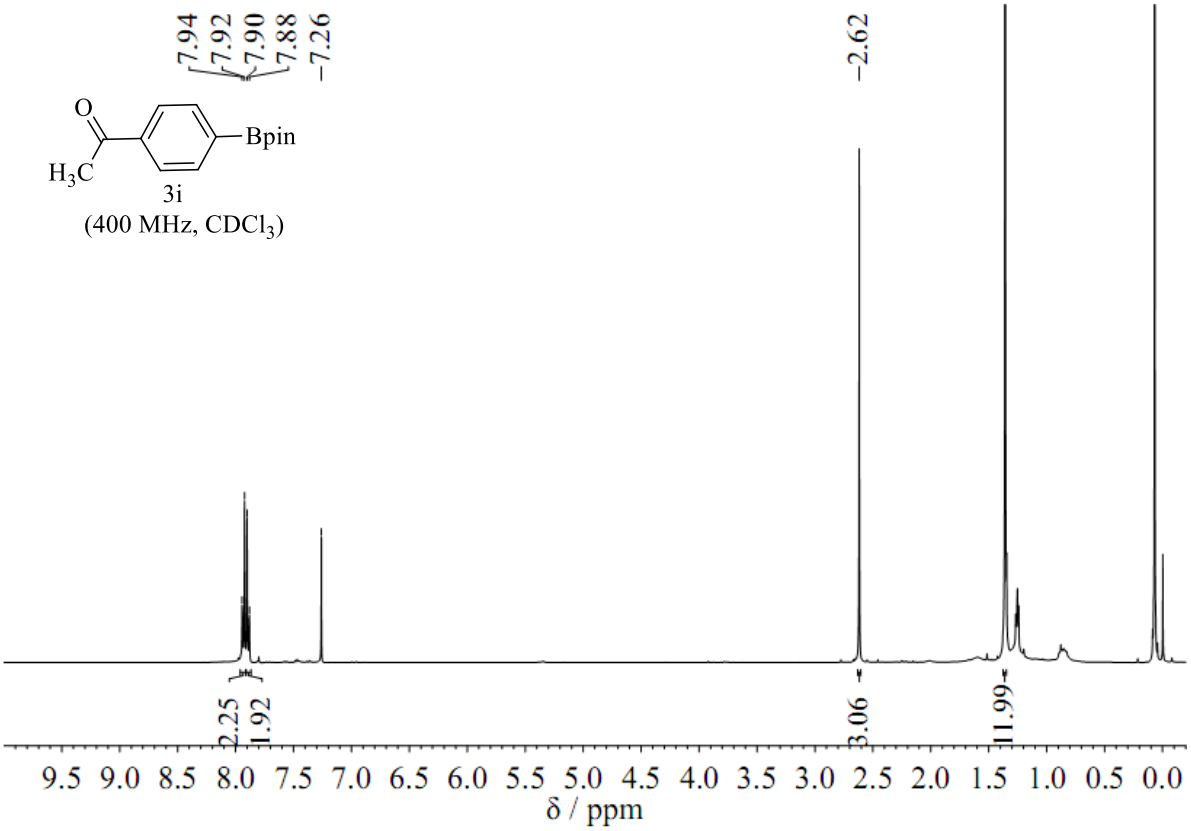

137.54
136.13
128.02
84.02
77.35
77.03
76.71
24.87
Cl
Bpin
3g
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

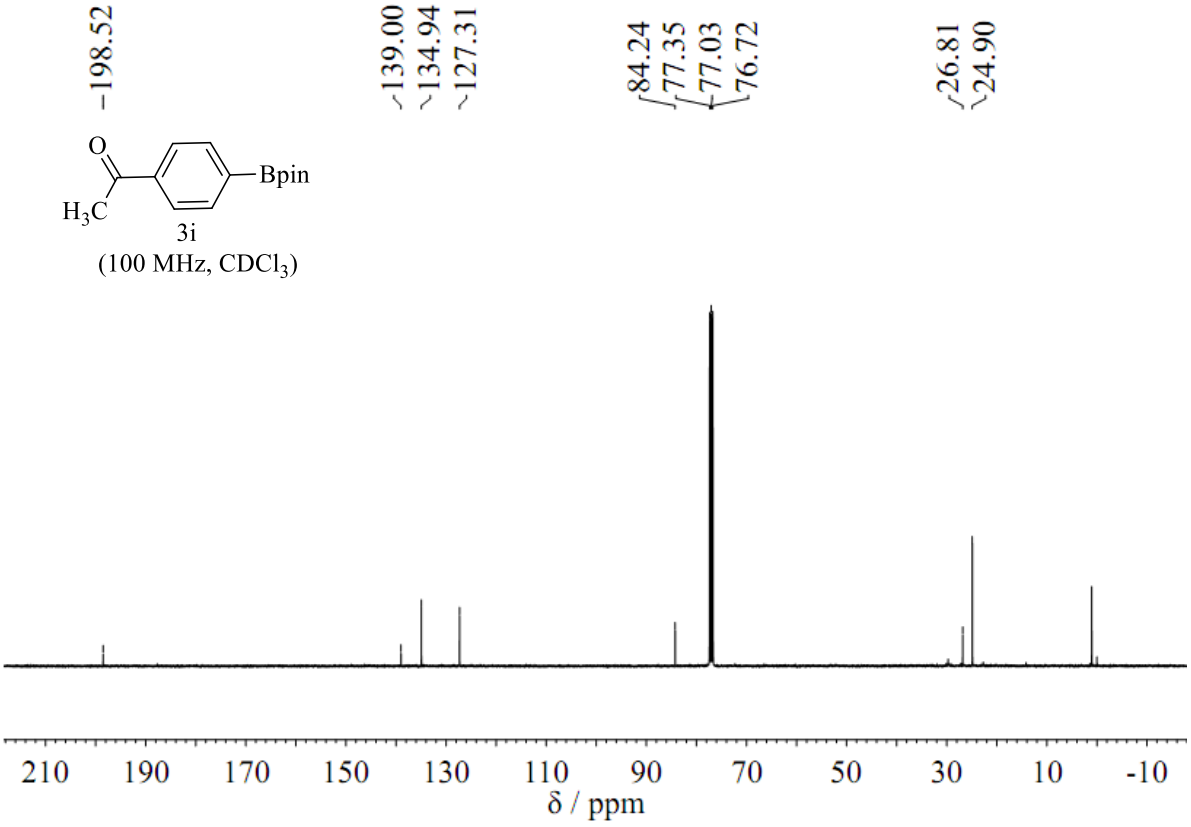


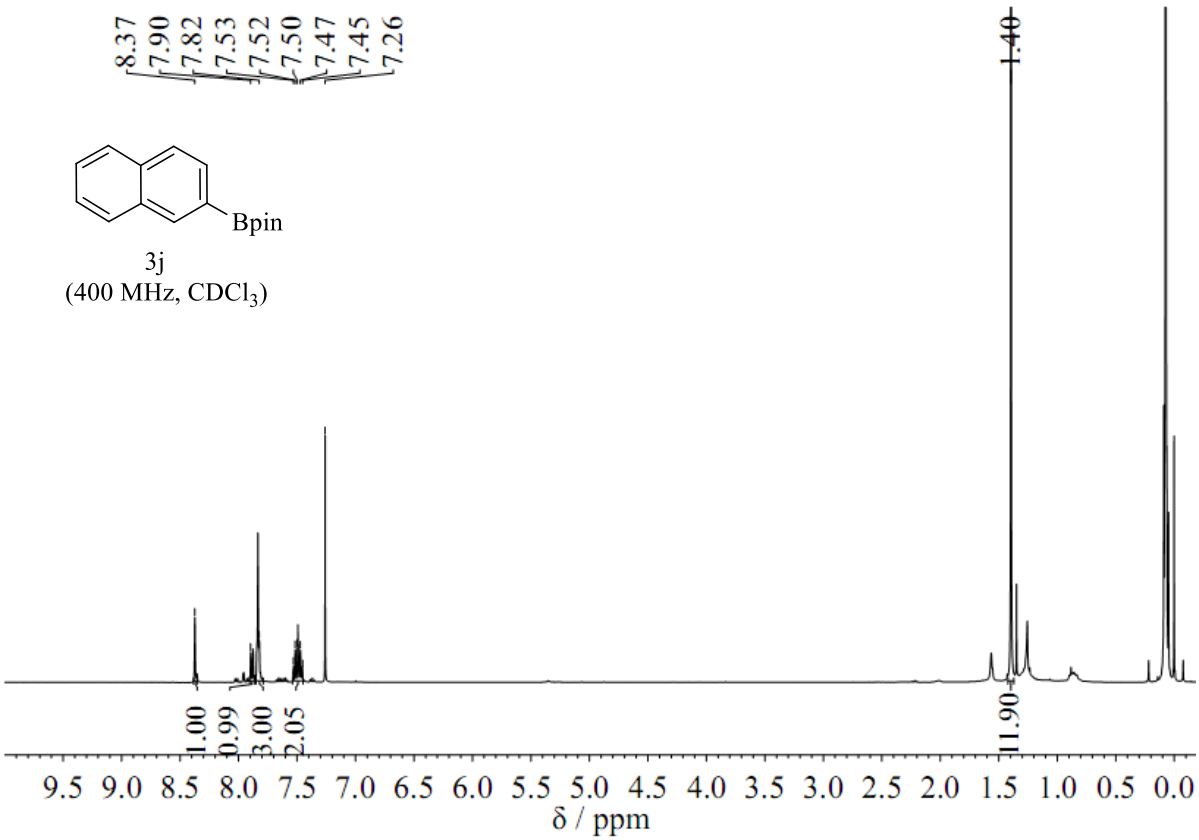
3h
(400 MHz, $CDCl_3$)

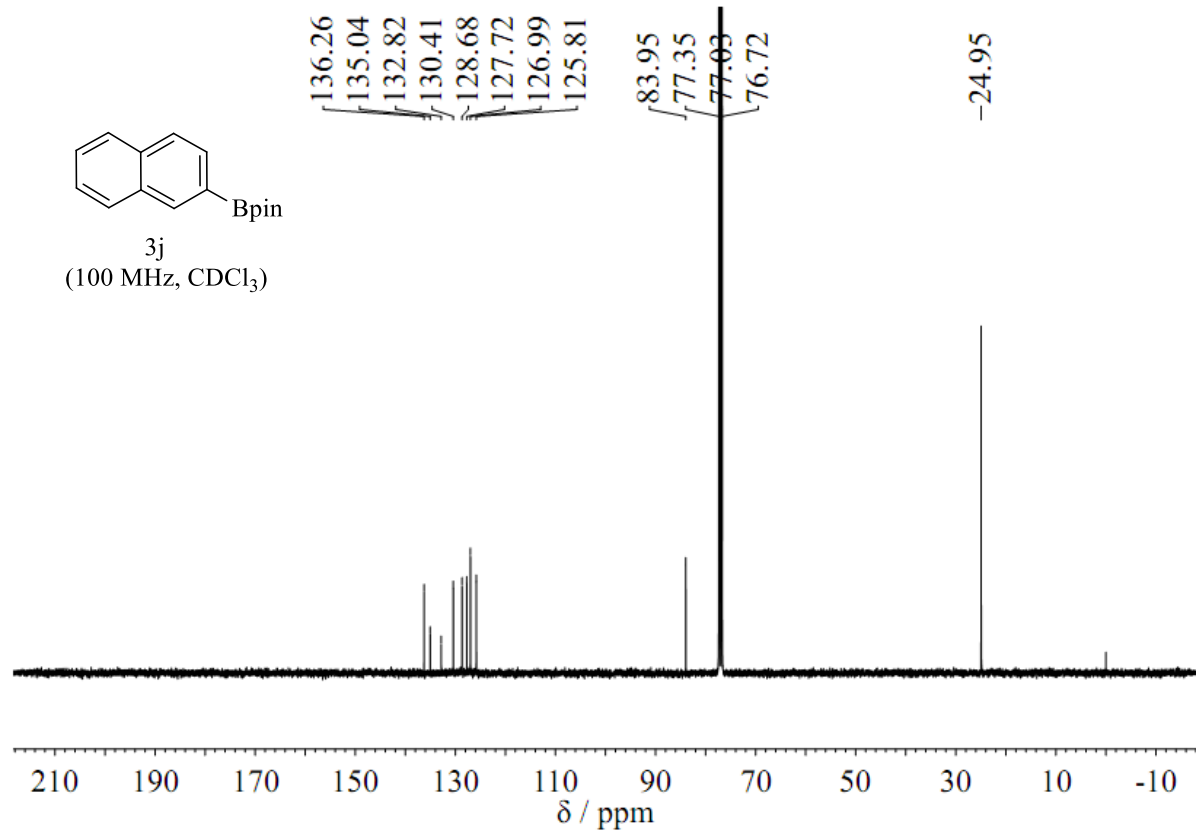


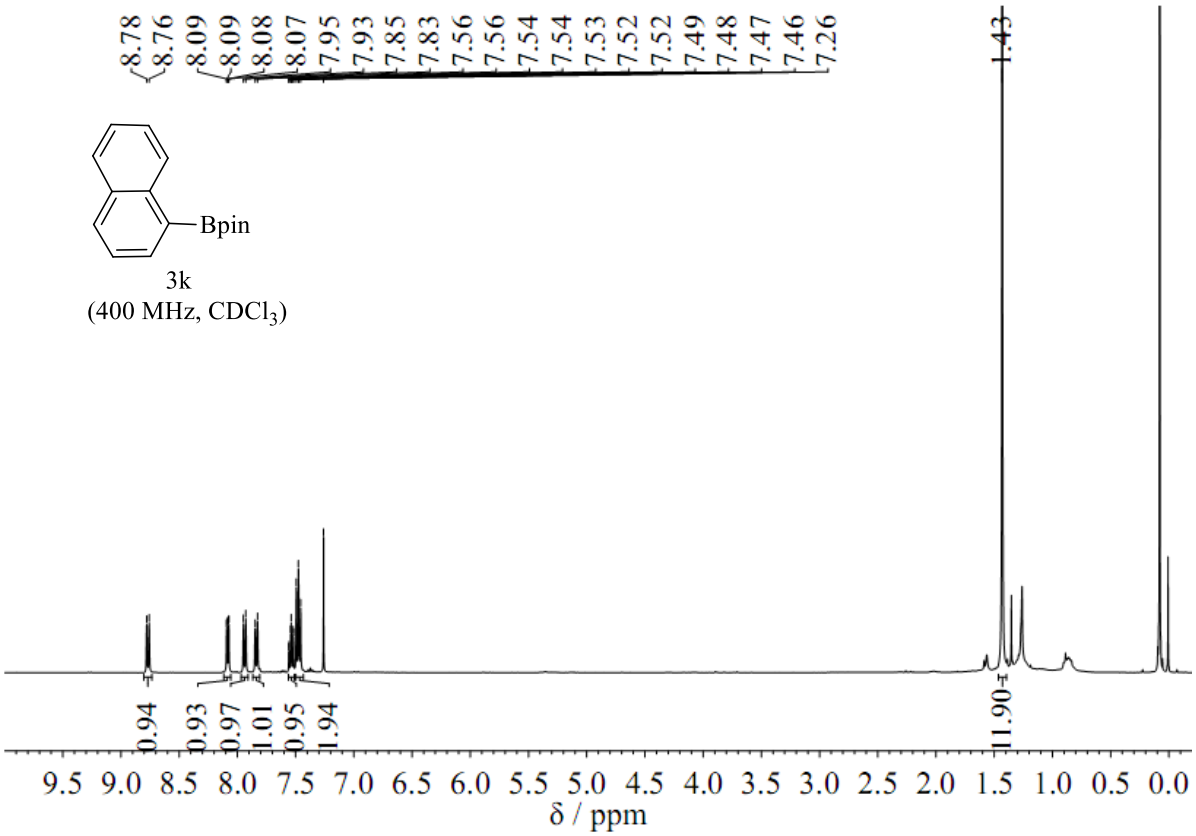
3h
(100 MHz, $CDCl_3$)

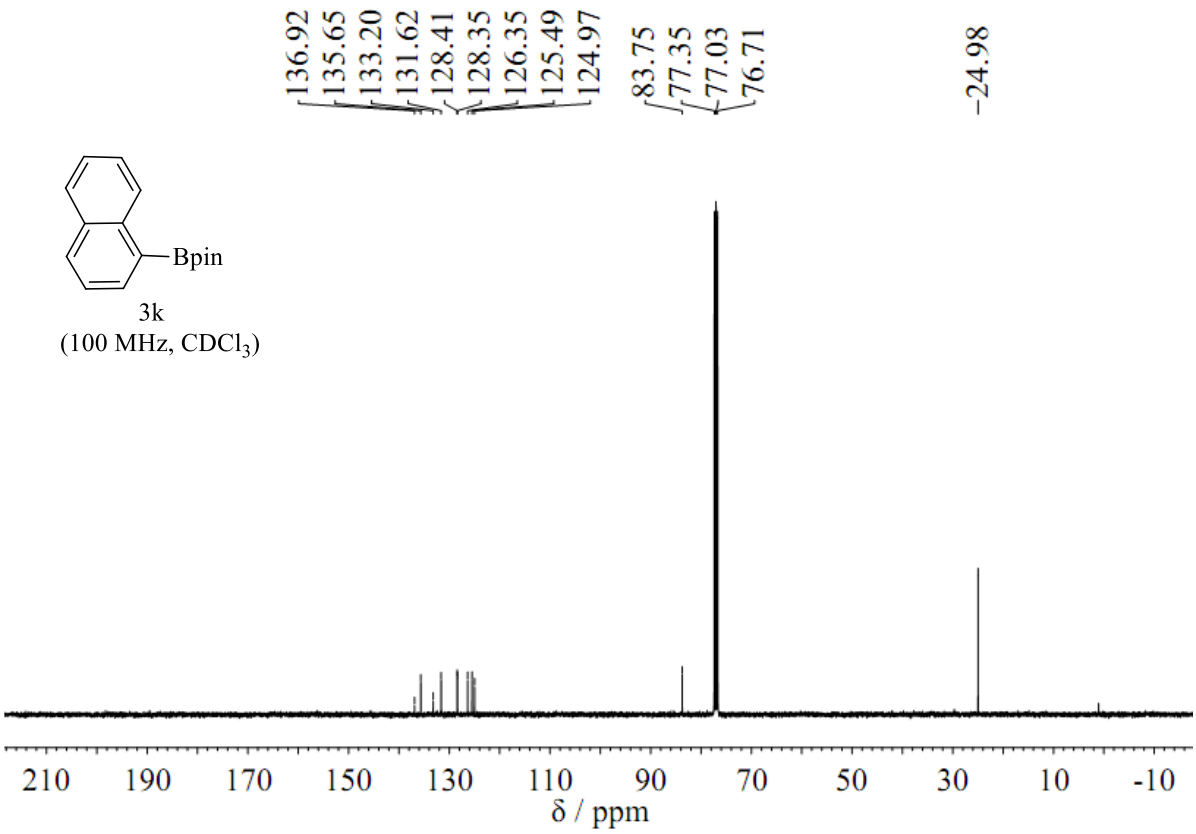

7.94
7.92
7.90
7.88
7.26
2.62
O
H3C
Bpin
3i
(400 MHz, CDCl3)
2.25
1.92
3.06
11.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

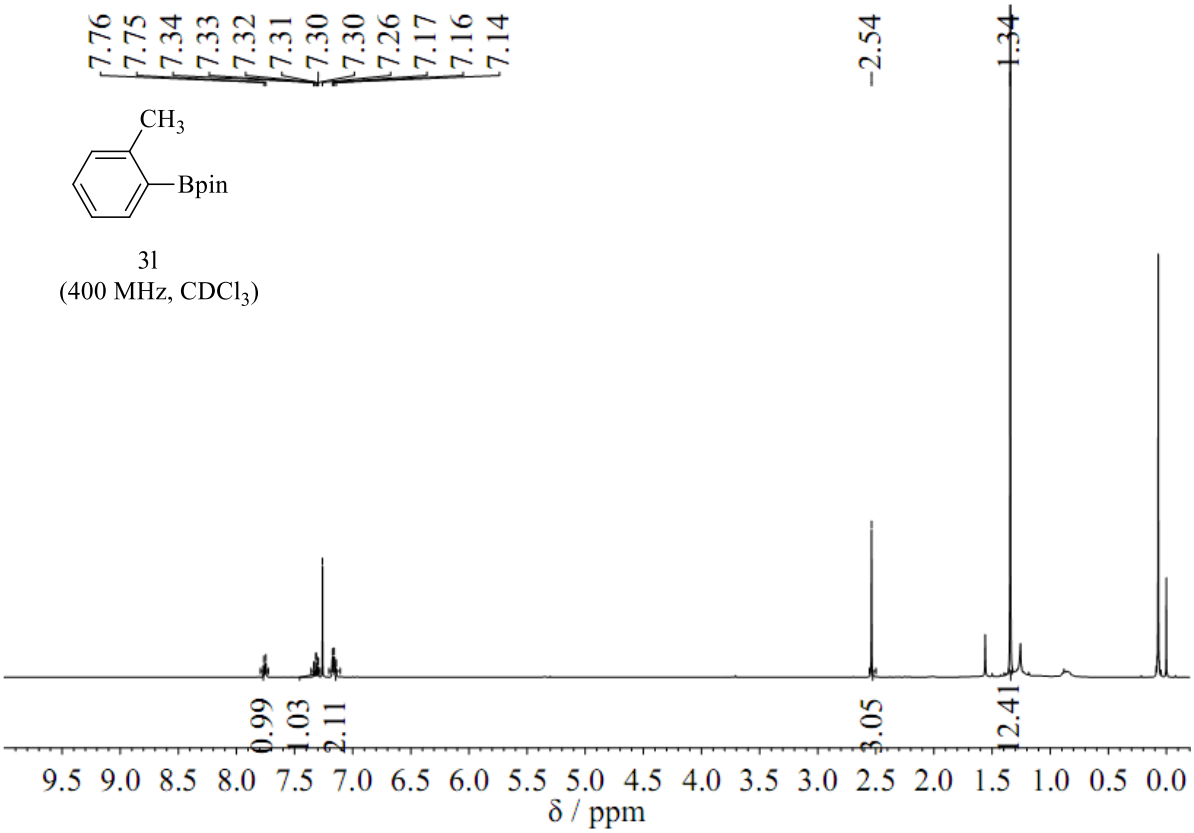

198.52
139.00
134.94
127.31
84.24
77.35
77.03
76.72
26.81
24.90
O
H3C
Bpin
3i
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.37
7.90
7.82
7.53
7.52
7.50
7.47
7.45
7.26
1.40
Bpin
3j
(400 MHz, CDCl3)
1.00
0.99
3.00
2.05
11.90
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
δ / ppm

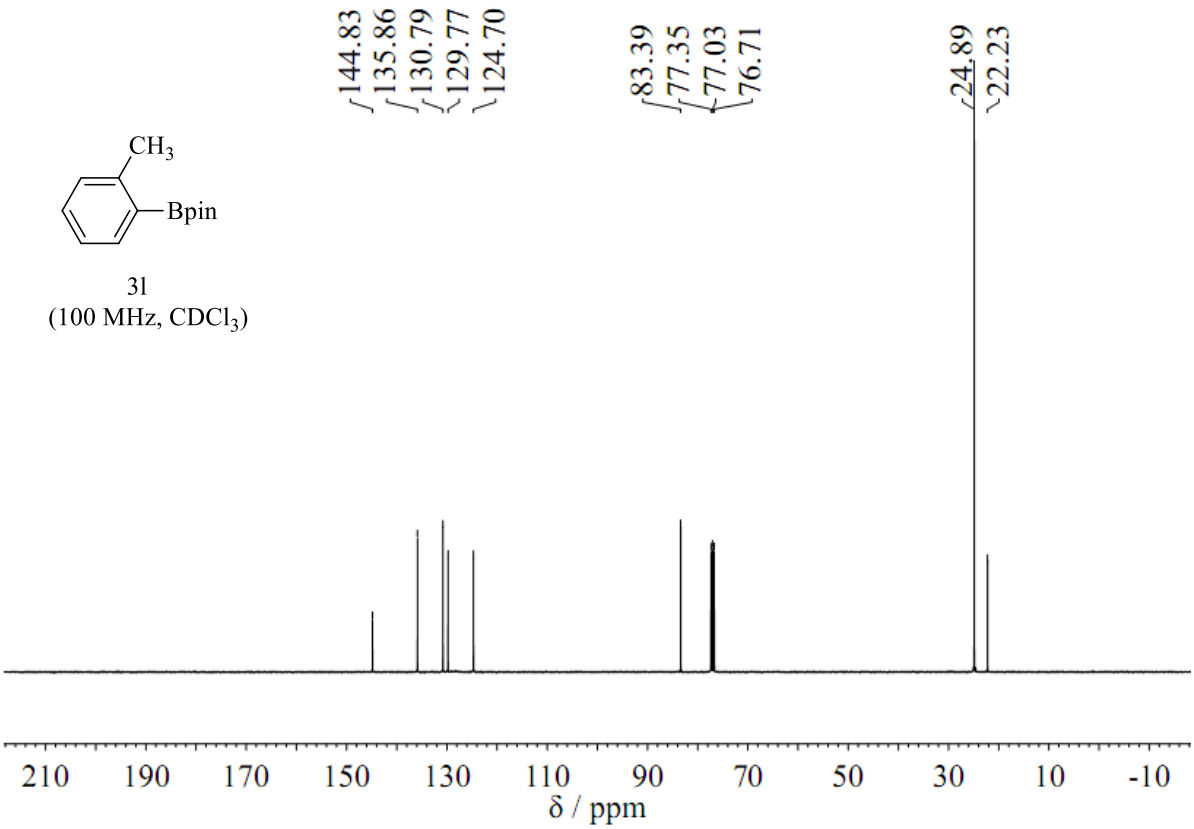

136.26
135.04
132.82
130.41
128.68
127.72
126.99
125.81
83.95
77.35
77.03
76.72
24.95
Bpin
3j
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.78
8.76
8.09
8.09
8.08
8.07
7.95
7.93
7.85
7.83
7.56
7.56
7.54
7.54
7.53
7.52
7.52
7.49
7.48
7.47
7.46
7.26
1.43
Bpin
3k
(400 MHz, CDCl3)
0.94
0.93
0.97
1.01
0.95
1.94
11.90
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
δ / ppm

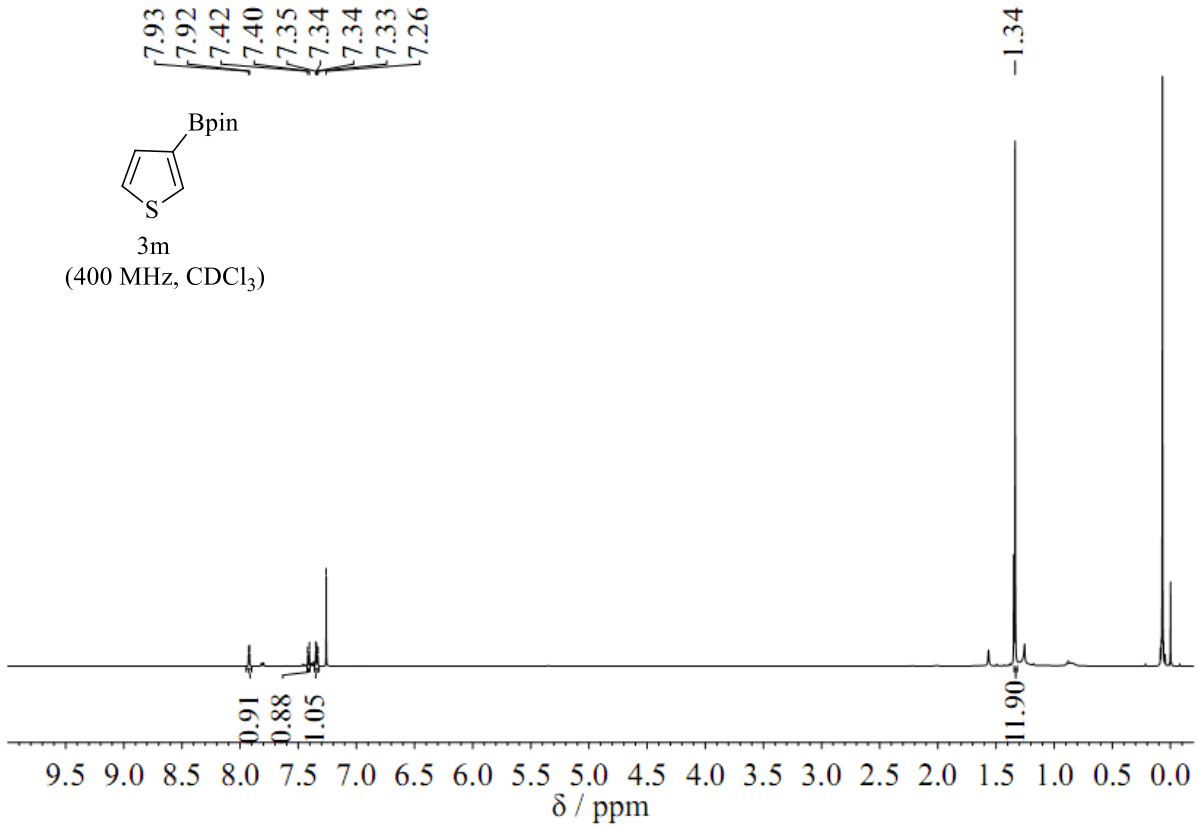

136.92
135.65
133.20
131.62
128.41
128.35
126.35
125.49
124.97
83.75
77.35
77.03
76.71
24.98
Bpin
3k
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

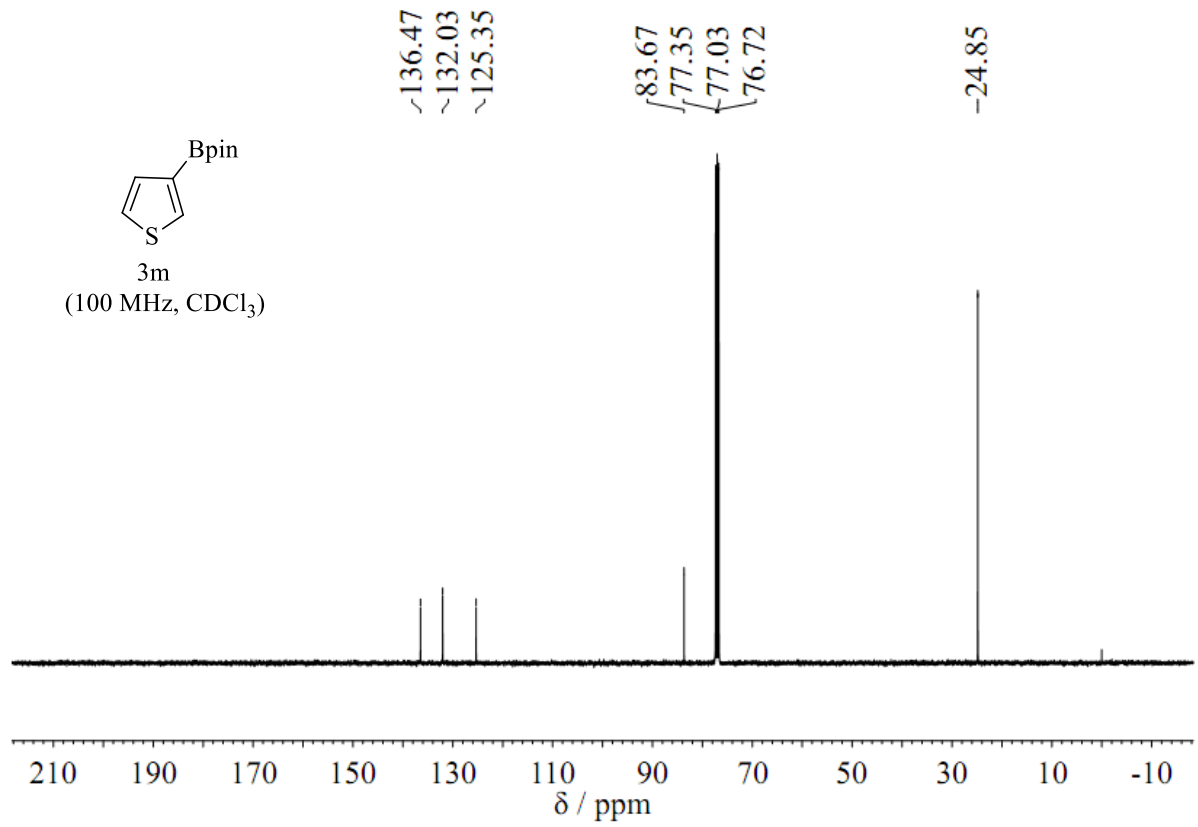


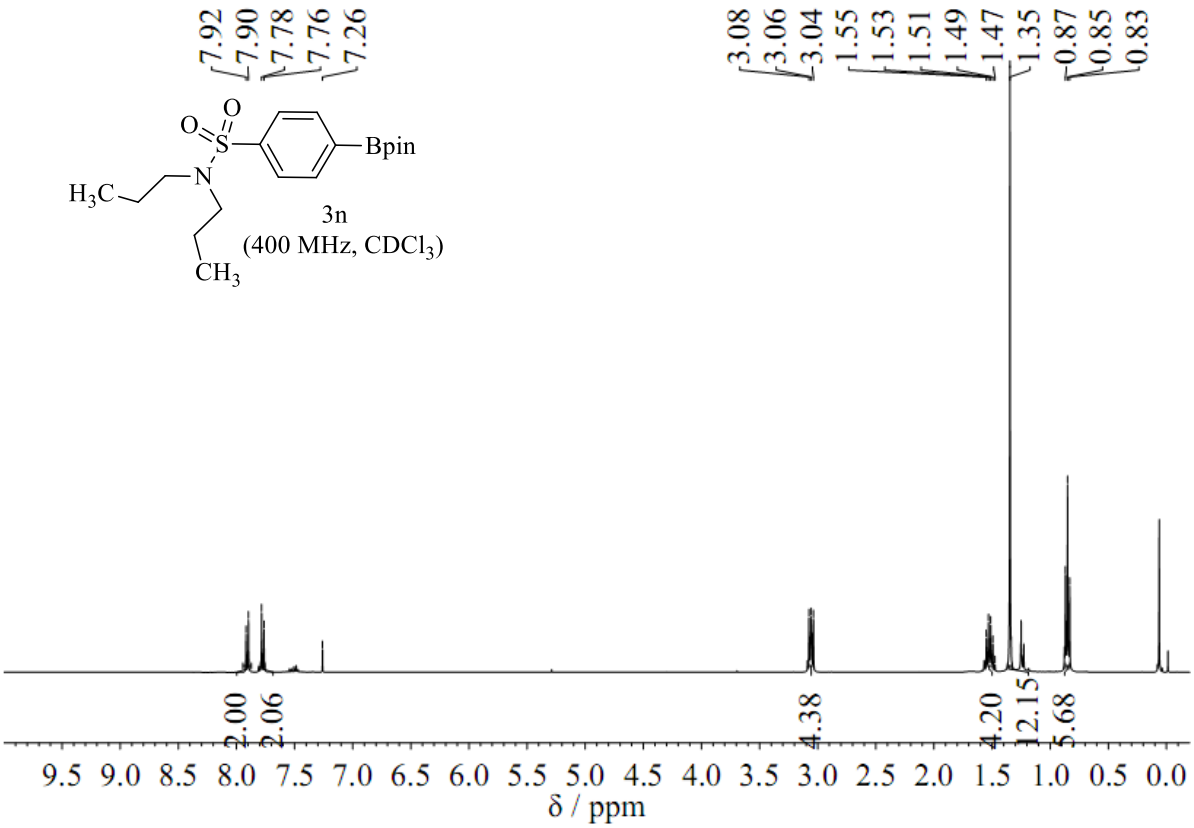
3l
(400 MHz, $CDCl_3$)

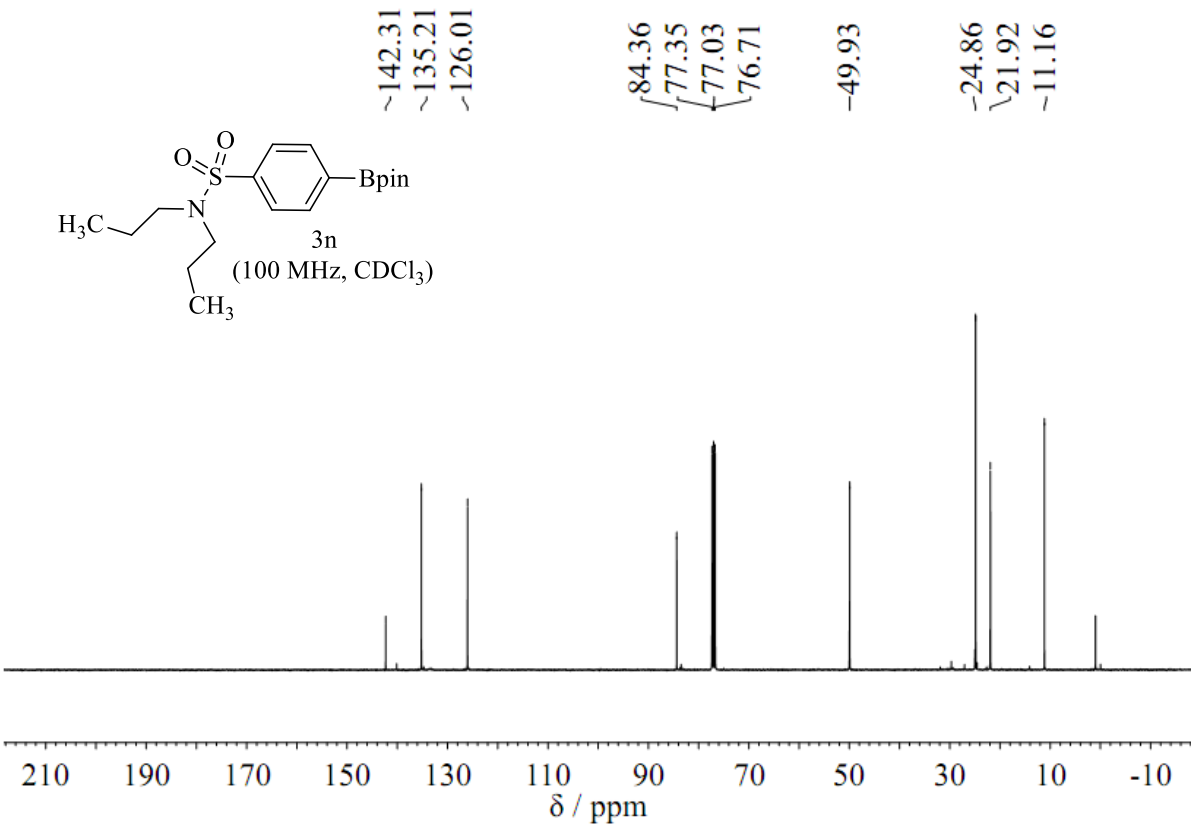


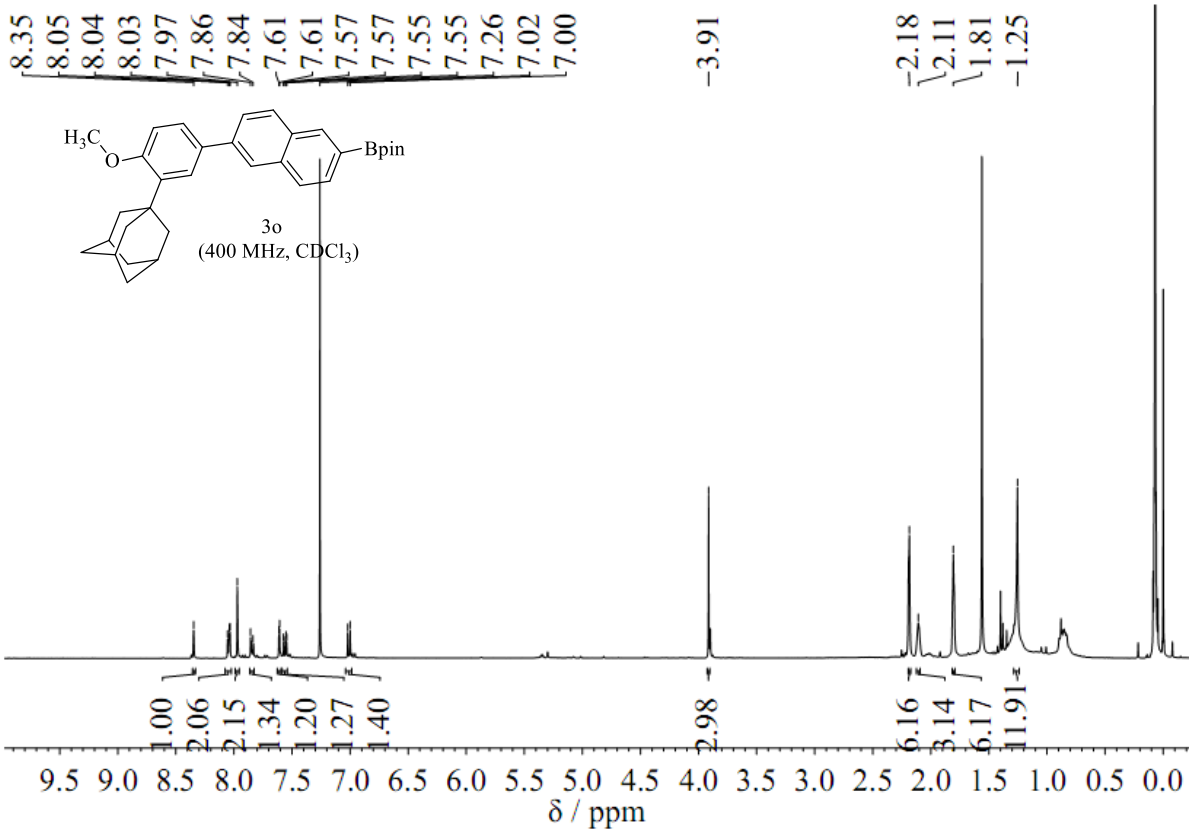
3l
(100 MHz, $CDCl_3$)

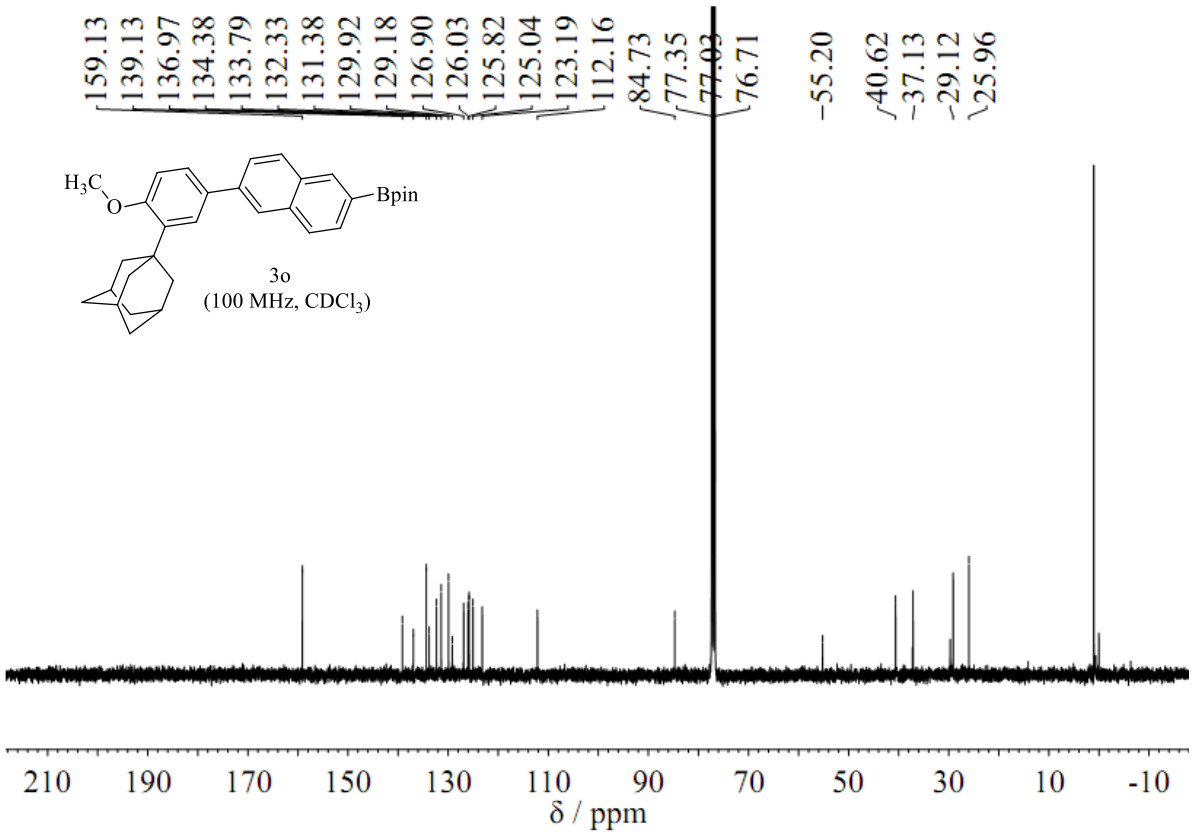

7.93
7.92
7.42
7.40
7.35
7.34
7.34
7.33
7.26
1.34
Bpin
S
3m
(400 MHz, CDCl3)
0.91
0.88
1.05
11.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

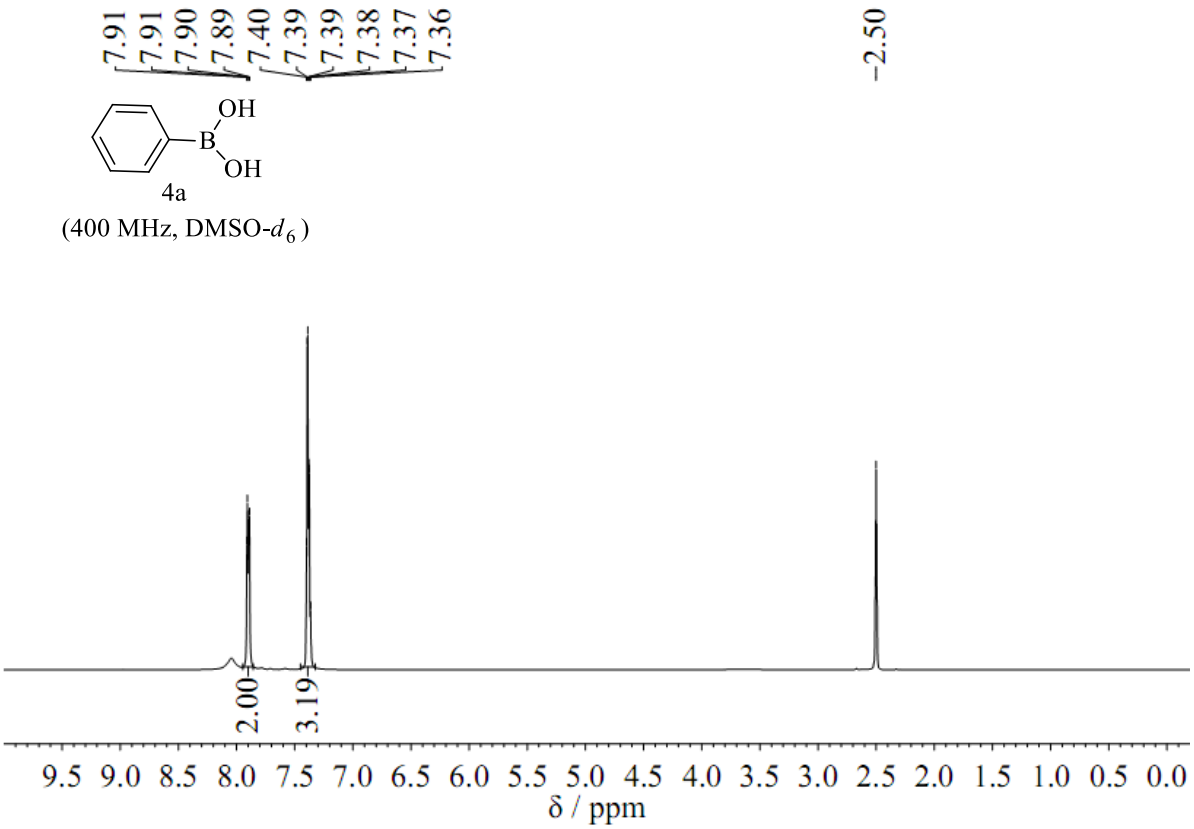

136.47
132.03
125.35
83.67
77.35
77.03
76.72
24.85
Bpin
S
3m
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


7.92
7.90
7.78
7.76
7.26
3.08
3.06
3.04
1.55
1.53
1.51
1.49
1.47
1.35
0.87
0.85
0.83
Bpin
H_3C
CH_3
3n
(400 MHz, $CDCl_3$)
2.00
2.06
4.38
4.20
12.15
5.68
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
δ / ppm


142.31
135.21
126.01
84.36
77.35
77.03
76.71
49.93
24.86
21.92
11.16
Bpin
H_3C
CH_3
3n
(100 MHz, $CDCl_3$)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

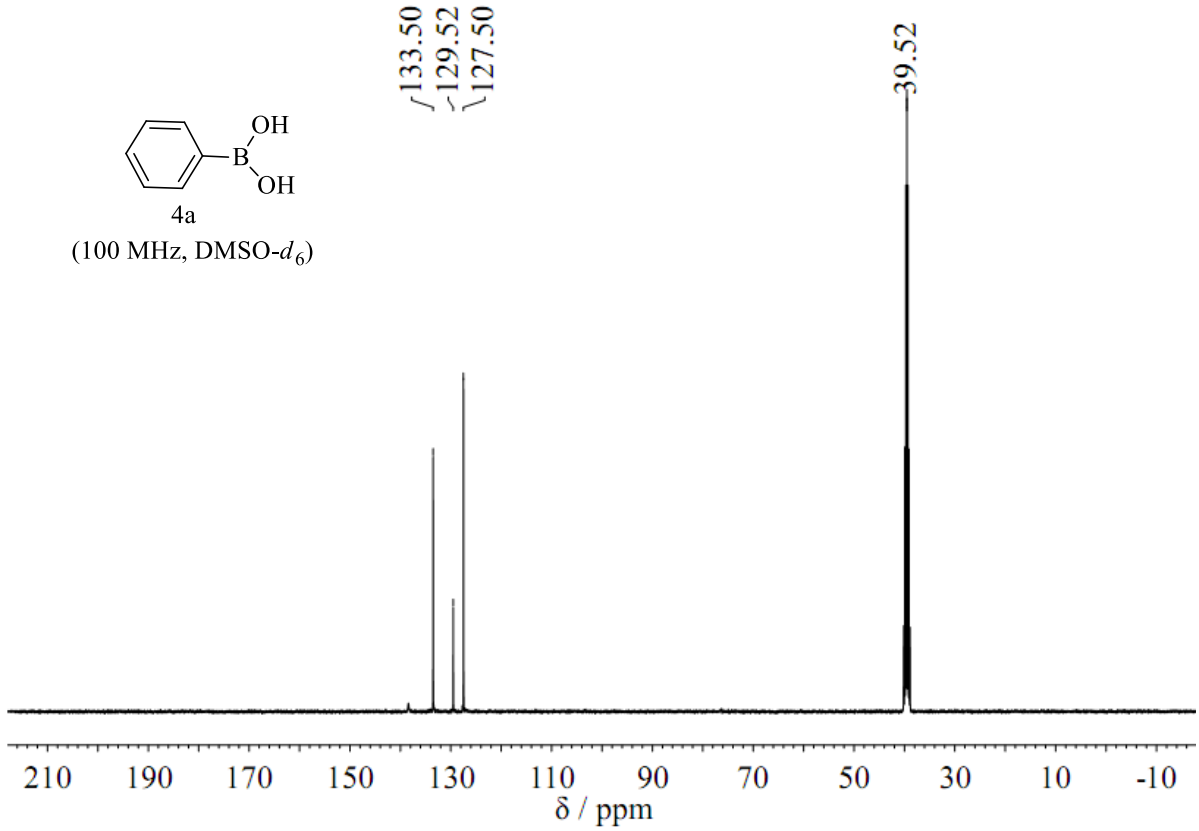

8.35
8.05
8.04
8.03
7.97
7.86
7.84
7.61
7.61
7.57
7.57
7.55
7.55
7.26
7.02
7.00
3.91
2.18
2.11
1.81
1.25
H3C
O
Bpin
3o
(400 MHz, CDCl3)
1.00
2.06
2.15
1.34
1.20
1.27
1.40
2.98
6.16
3.14
6.17
11.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm


159.13
139.13
136.97
134.38
133.79
132.33
131.38
129.92
129.18
126.90
126.03
125.82
125.04
123.19
112.16
84.73
77.35
77.03
76.71
55.20
40.62
37.13
29.12
25.96
H3C
O
Bpin
3o
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



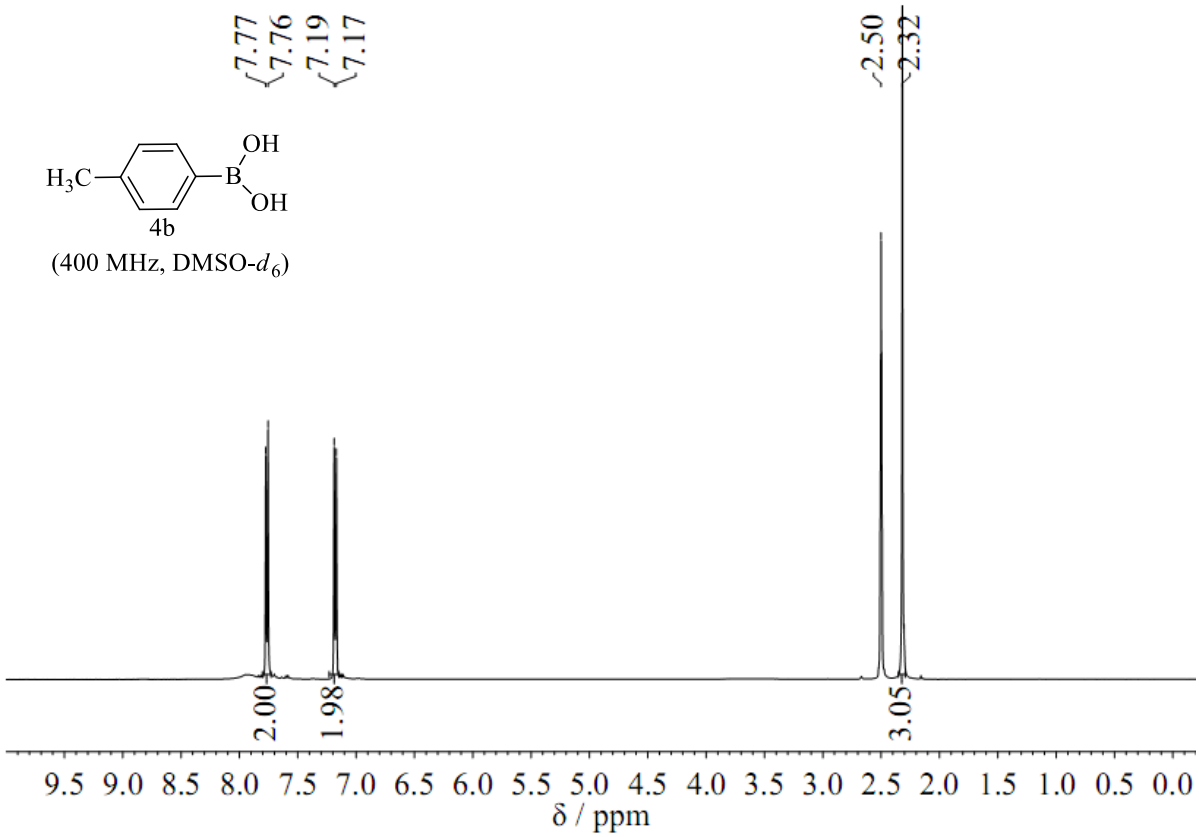
4a

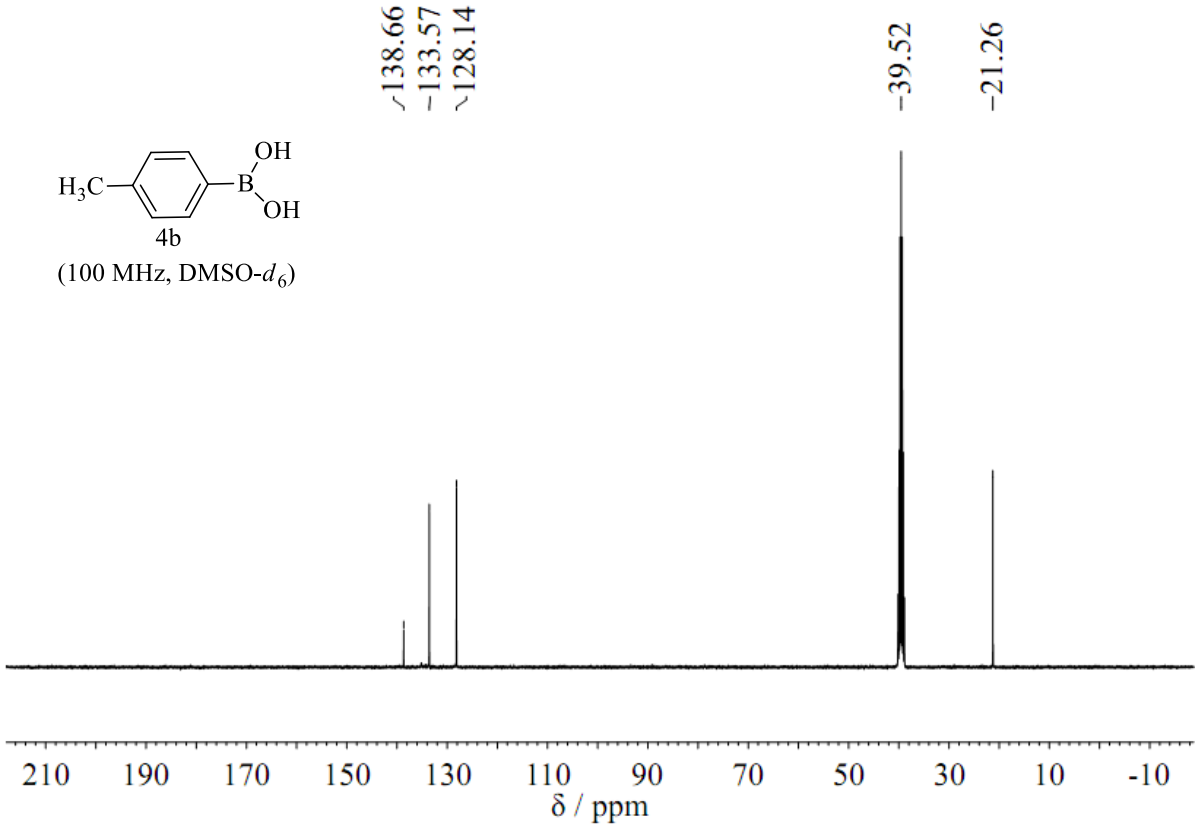
(400 MHz, DMSO-d_6)

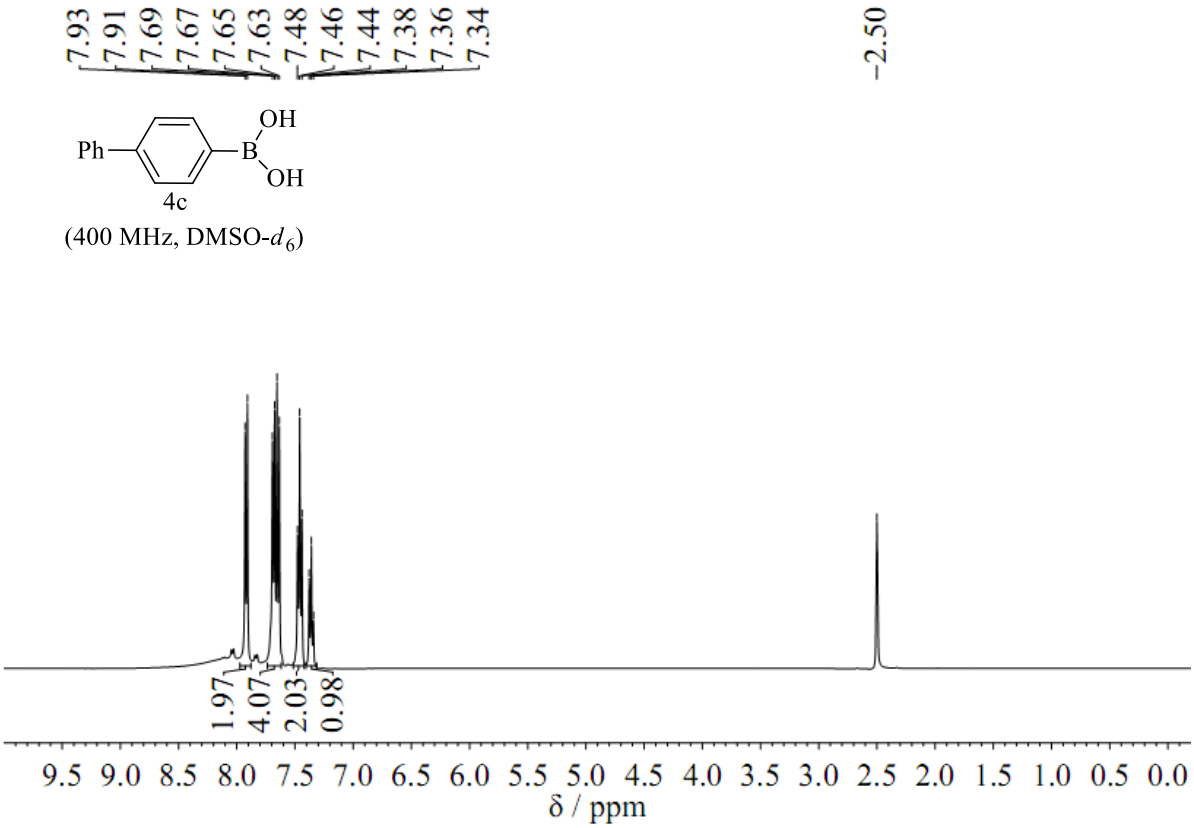


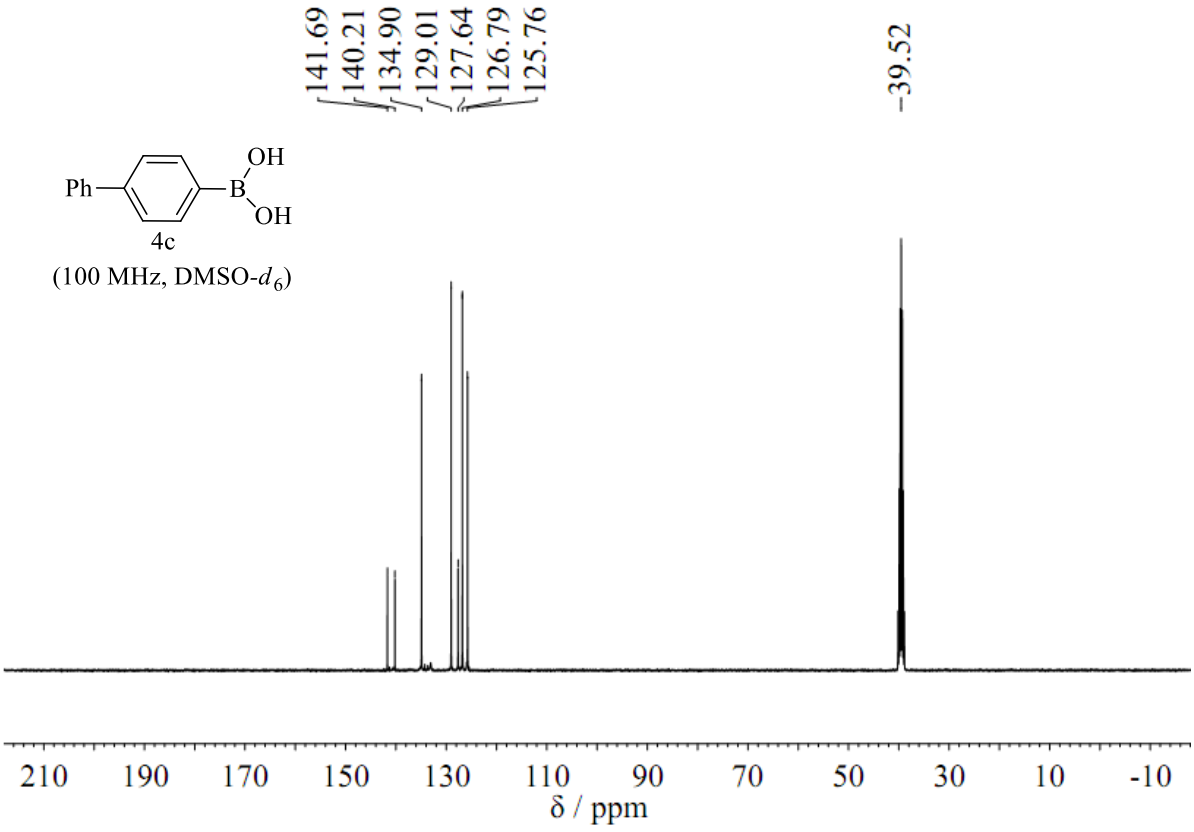
4a

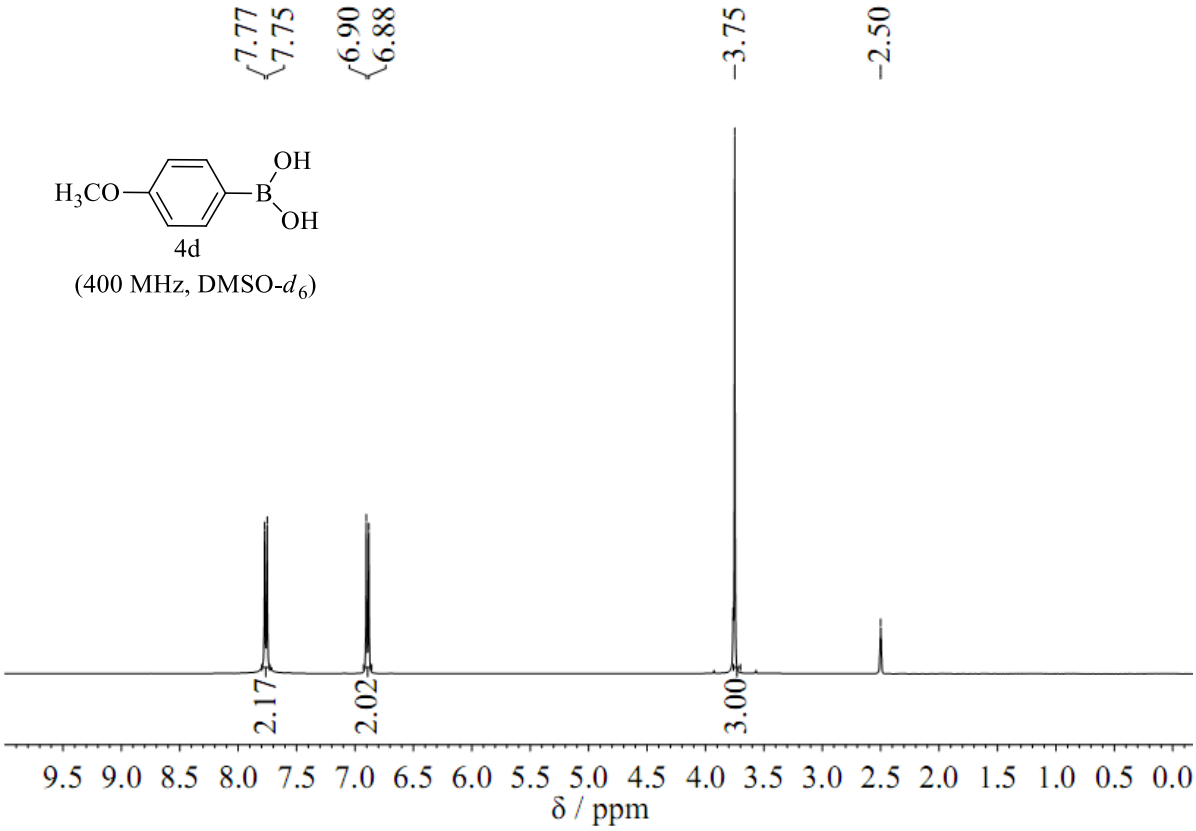
(100 MHz, DMSO-d_6)


7.77
7.76
7.19
7.17
2.50
2.32
OH
H_3C
B
OH
4b
(400 MHz, DMSO-d_6)
2.00
1.98
3.05
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
δ / ppm


138.66
133.57
128.14
39.52
21.26
OH
H_3C
B
OH
4b
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

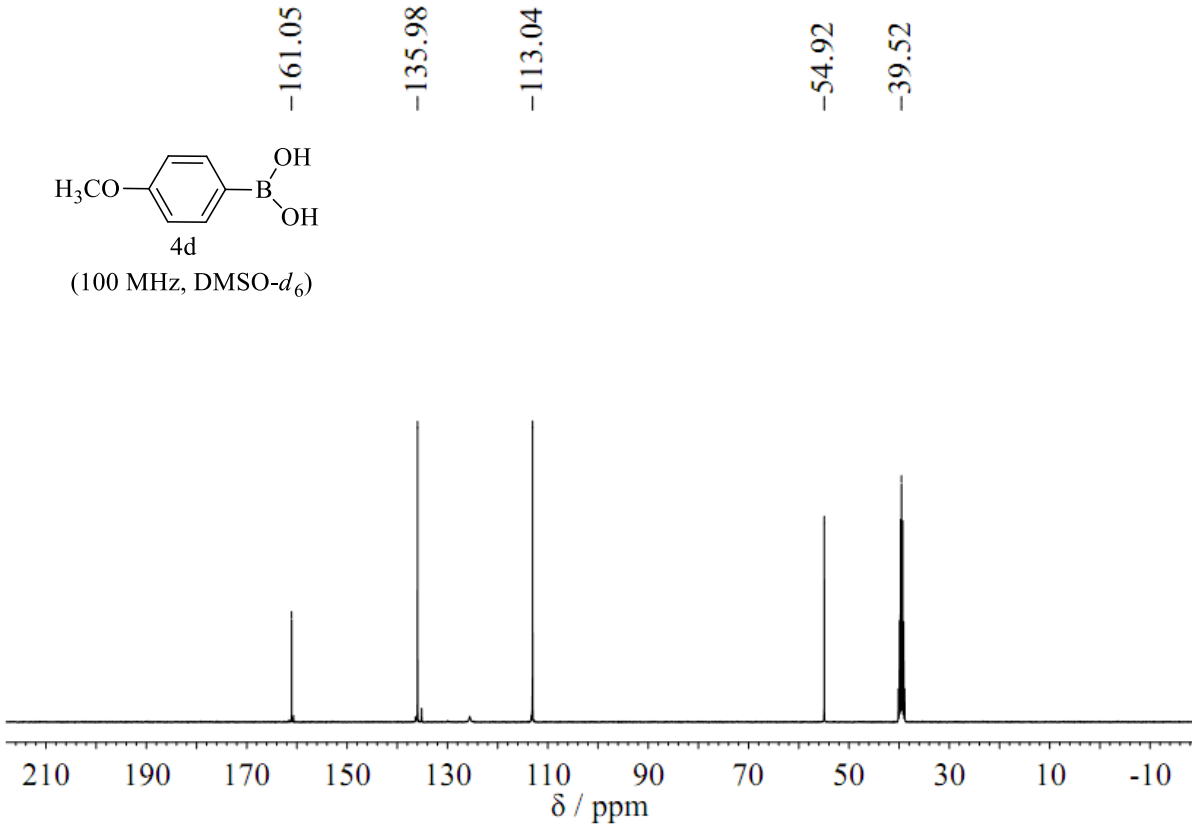

7.93
7.91
7.69
7.67
7.65
7.63
7.48
7.46
7.44
7.38
7.36
7.34
2.50
Ph
B
OH
OH
4c
(400 MHz, DMSO-d_6)
1.97
4.07
2.03
0.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm


141.69
140.21
134.90
129.01
127.64
126.79
125.76
39.52
Ph
B
OH
OH
4c
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



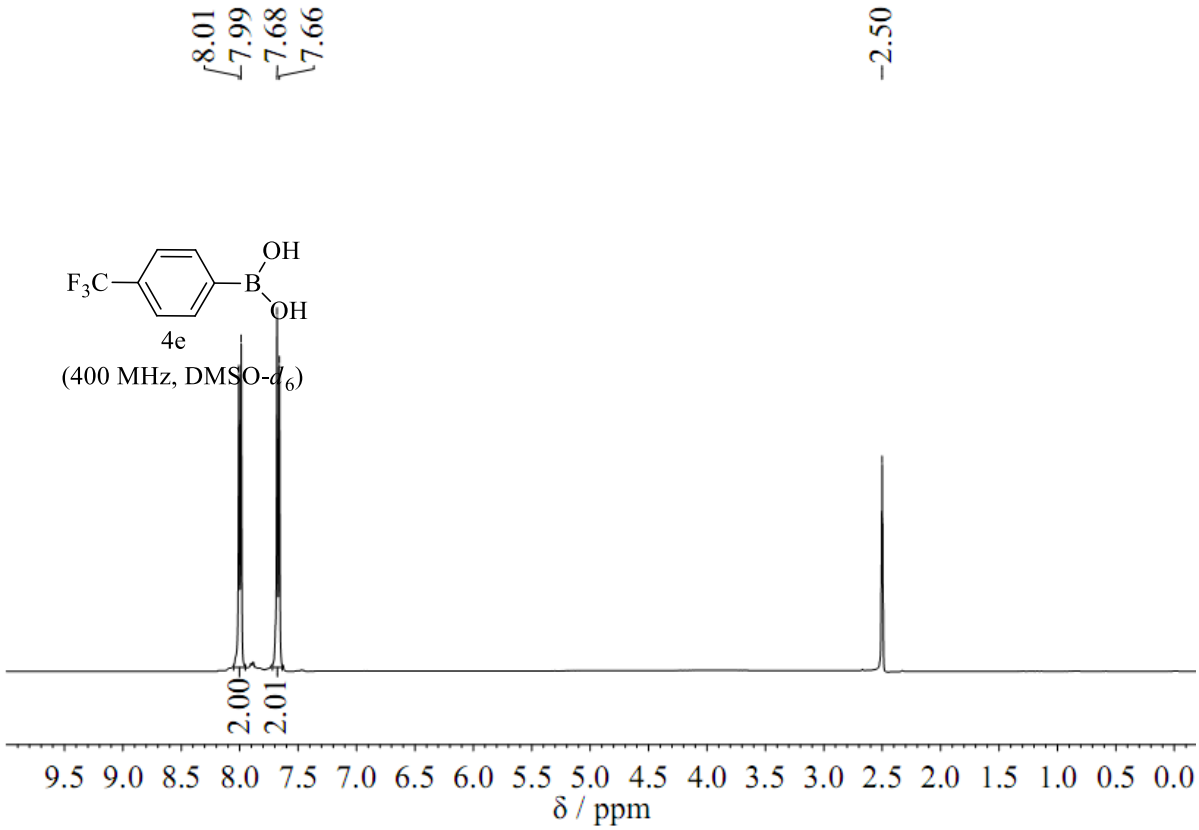
4d

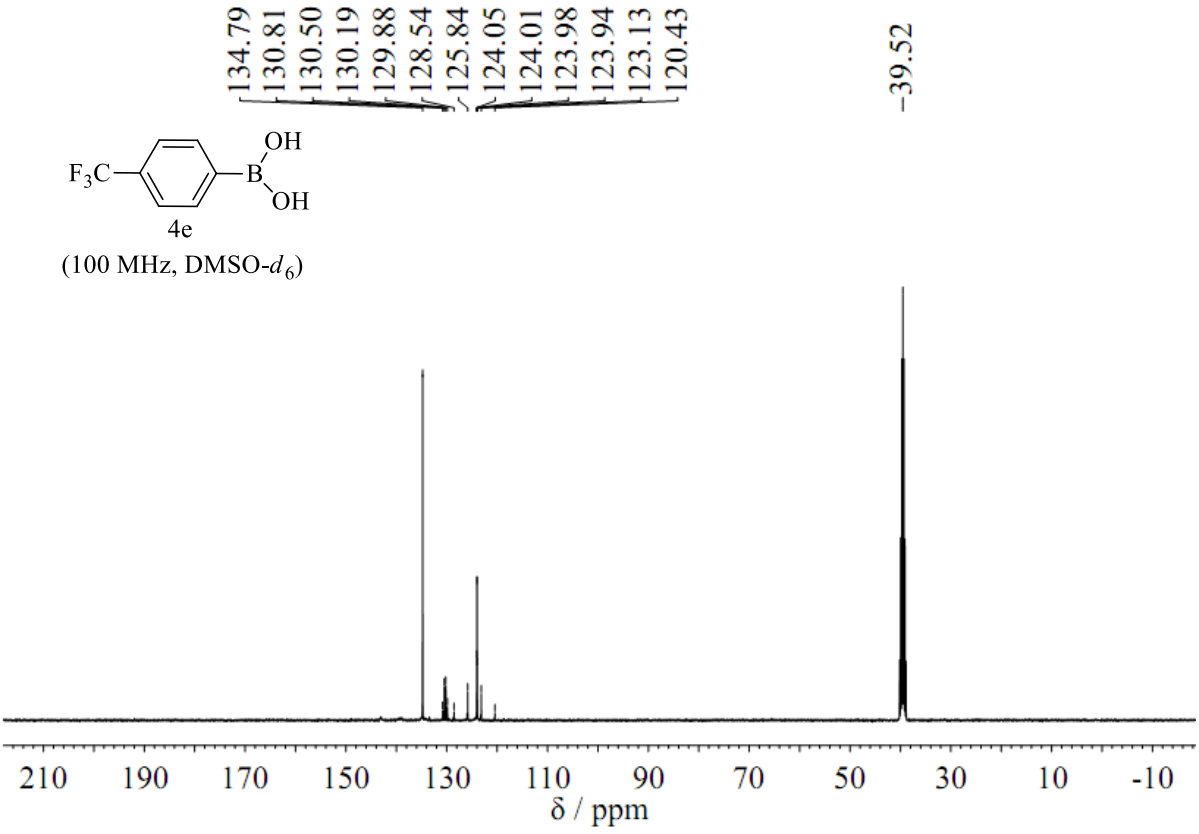
(400 MHz, DMSO-d_6)

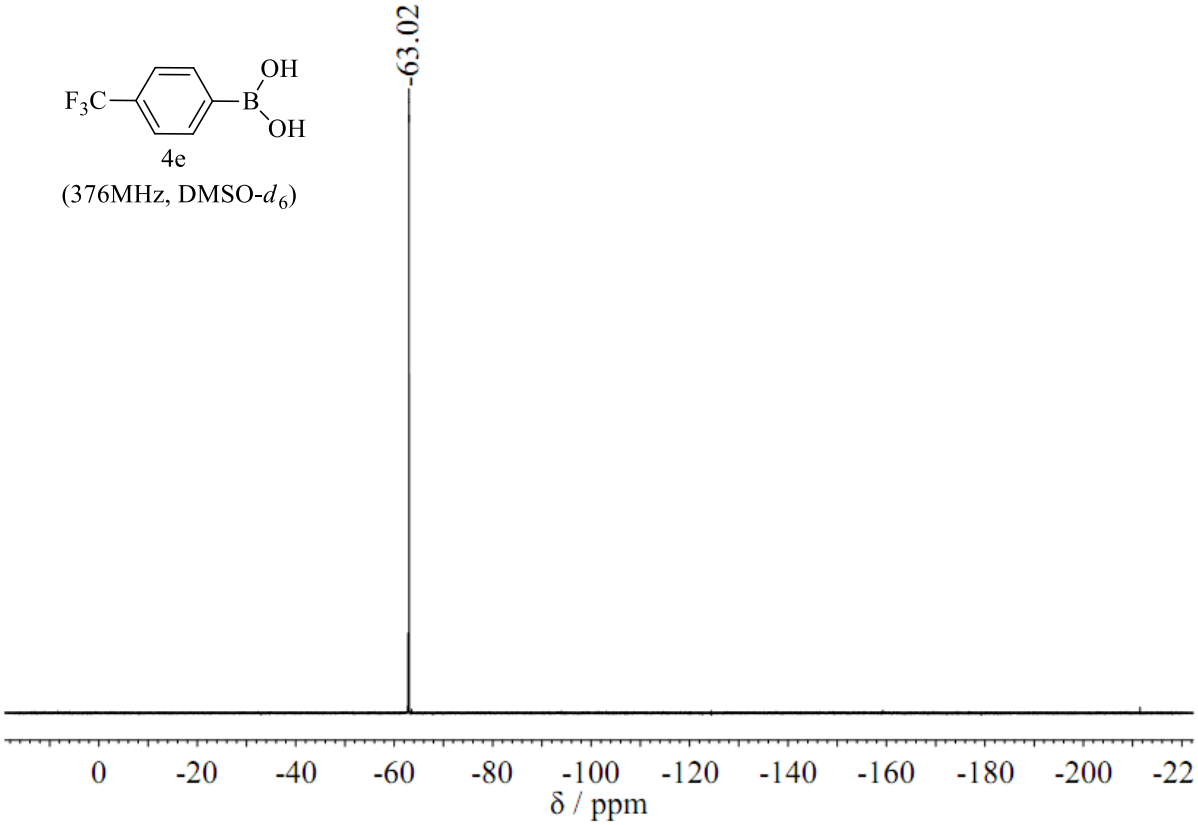


4d

(100 MHz, DMSO-d_6)

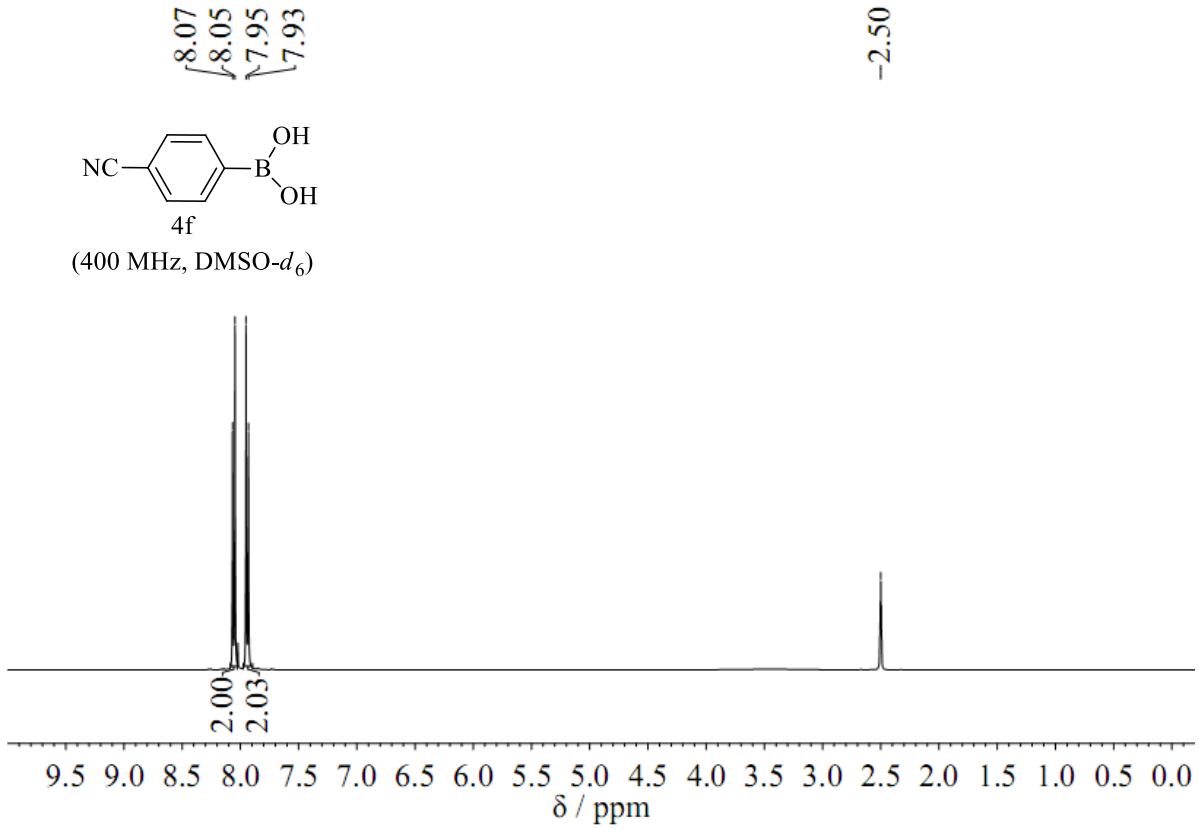

8.01
7.99
7.68
7.66
2.50
OH
B
OH
F_3C
4e
(400 MHz, DMSO-d_6)
2.00
2.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

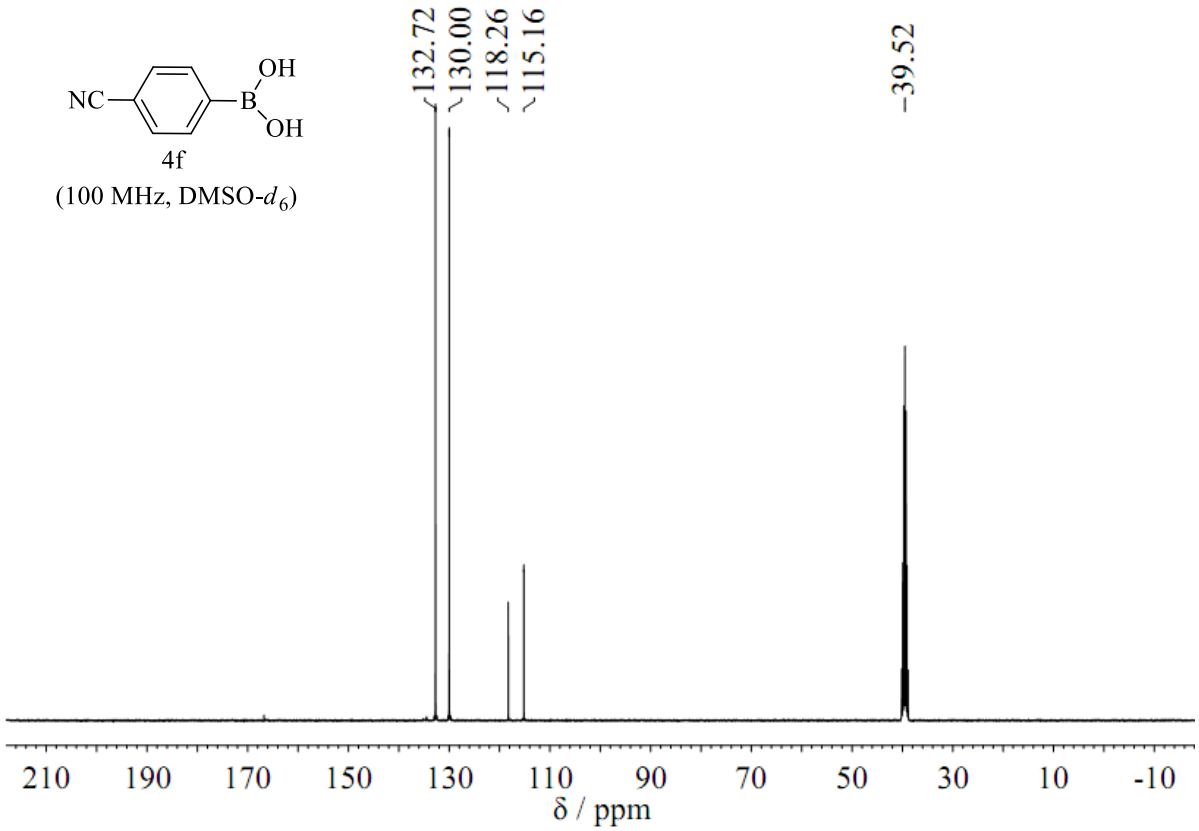

134.79
130.81
130.50
130.19
129.88
128.54
125.84
124.05
124.01
123.98
123.94
123.13
120.43
39.52
OH
B
OH
F_3C
4e
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

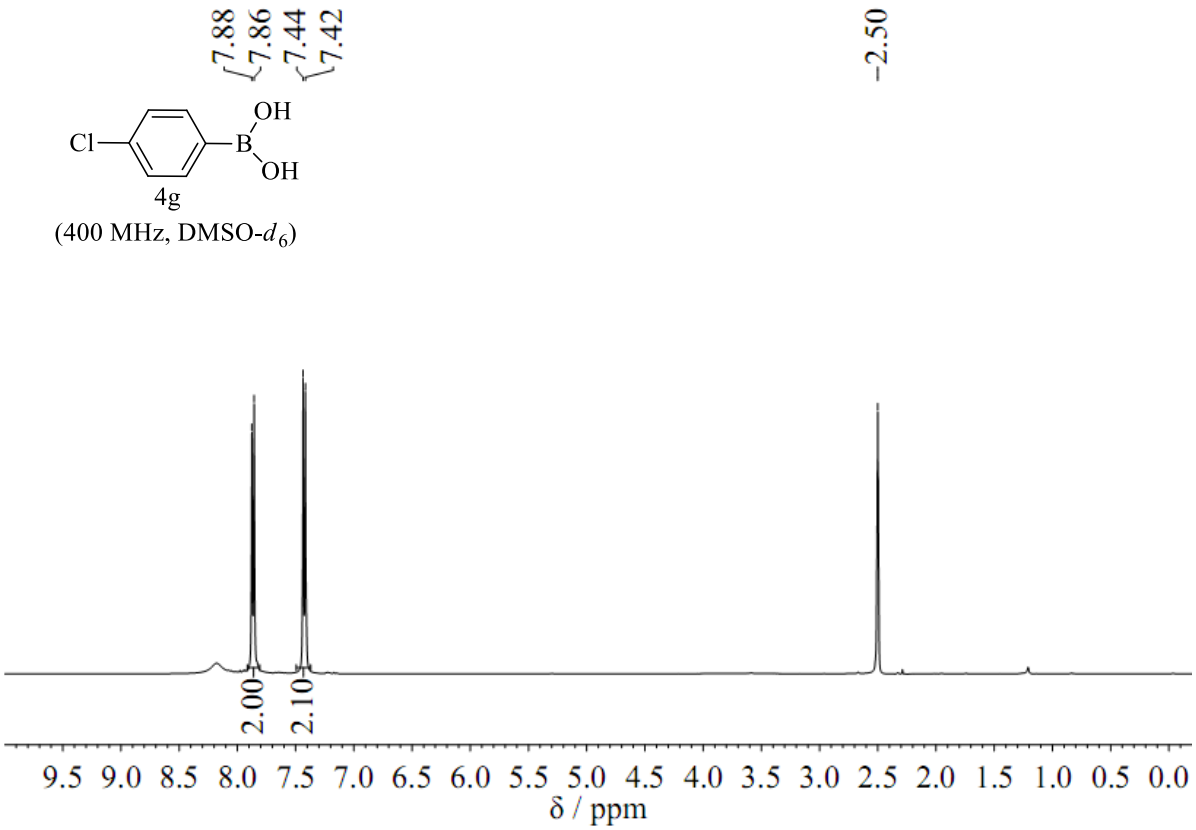


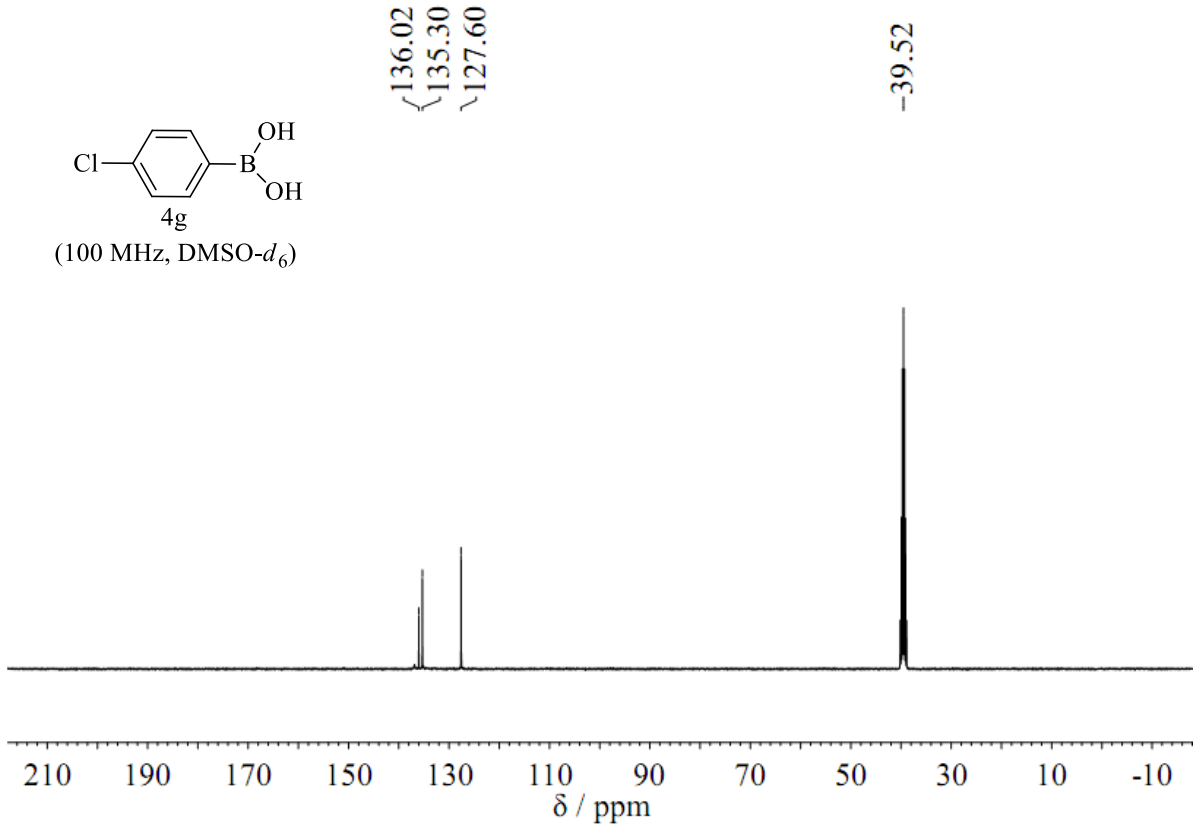
4e

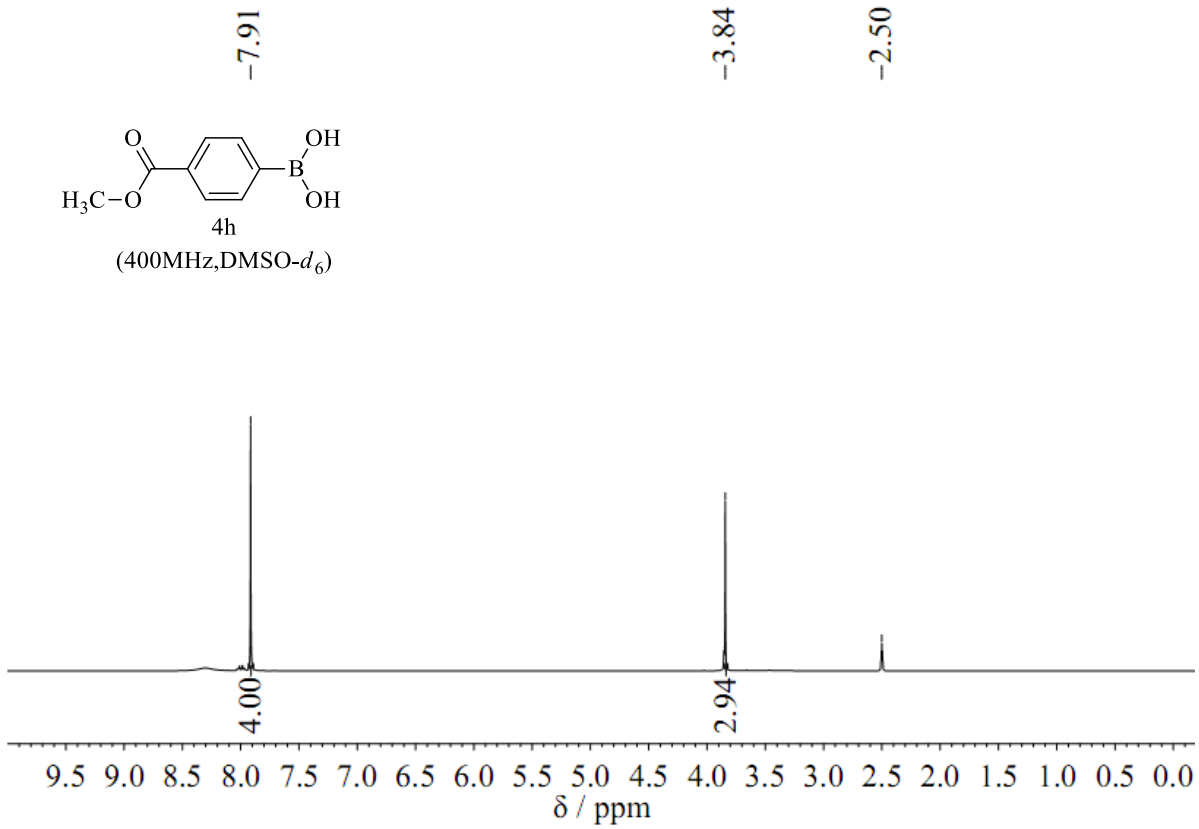
(376MHz, DMSO-d_6)

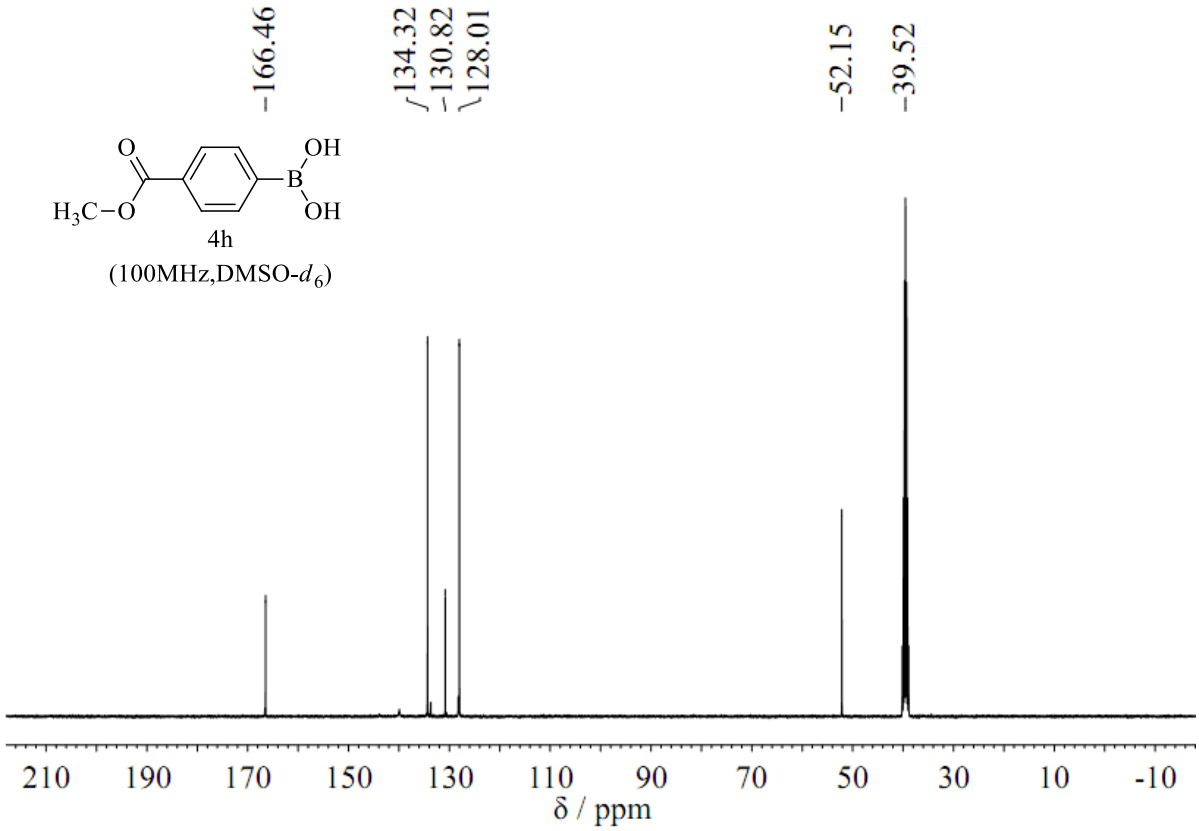

8.07
8.05
7.95
7.93
2.50
NC
B
OH
OH
4f
(400 MHz, DMSO-d_6)
2.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

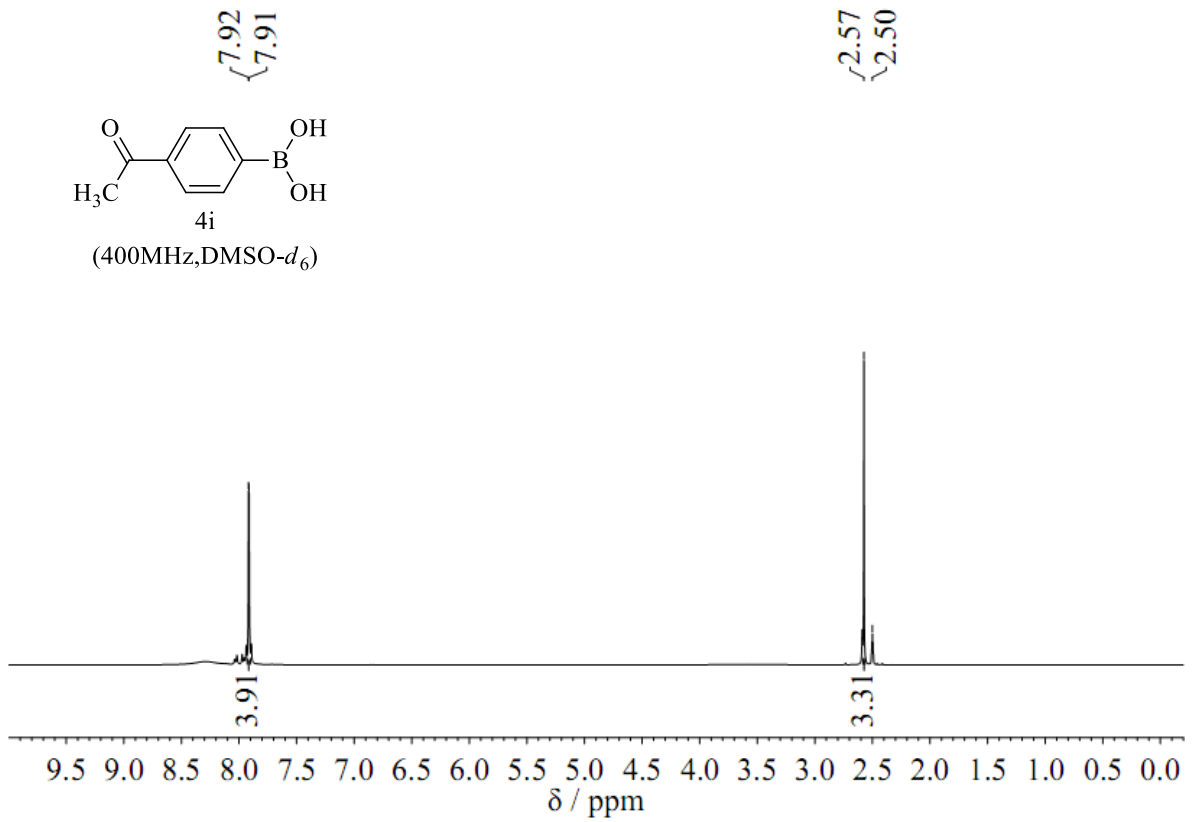

132.72
130.00
118.26
115.16
39.52
NC
B
OH
OH
4f
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

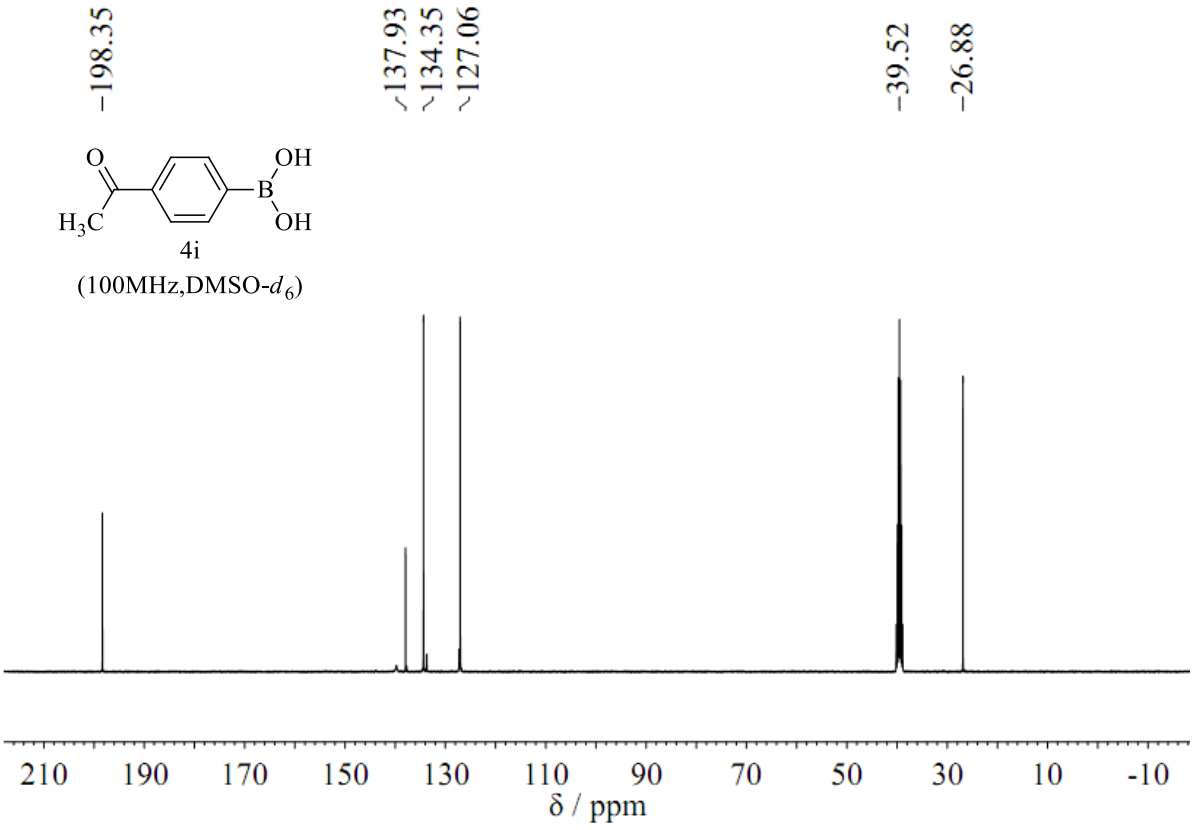

7.88
7.86
7.44
7.42
2.50
Cl
B
OH
OH
4g
(400 MHz, DMSO-d_6)
2.00
2.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

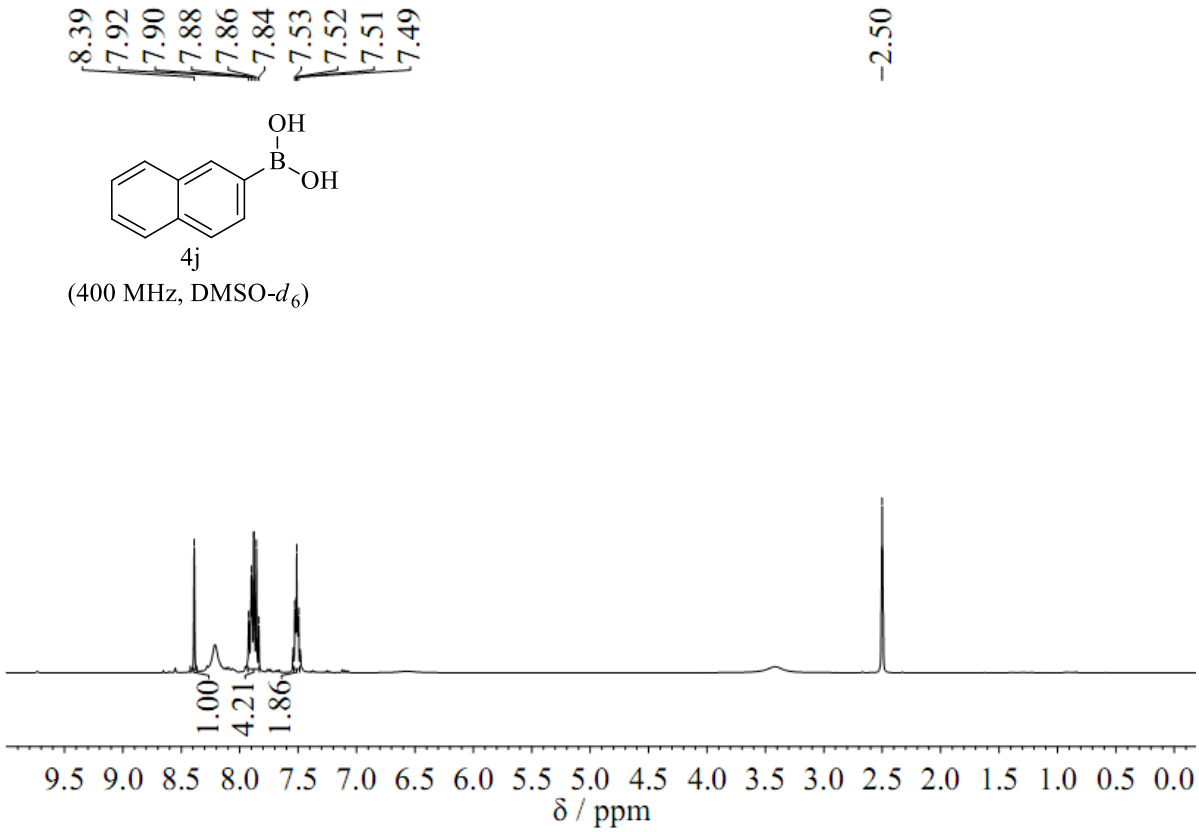

136.02
135.30
127.60
39.52
Cl
B
OH
OH
4g
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


7.91
3.84
2.50
O
OH
B
H3C−O
OH
4h
(400MHz,DMSO-d6)
4.00
2.94
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
δ / ppm

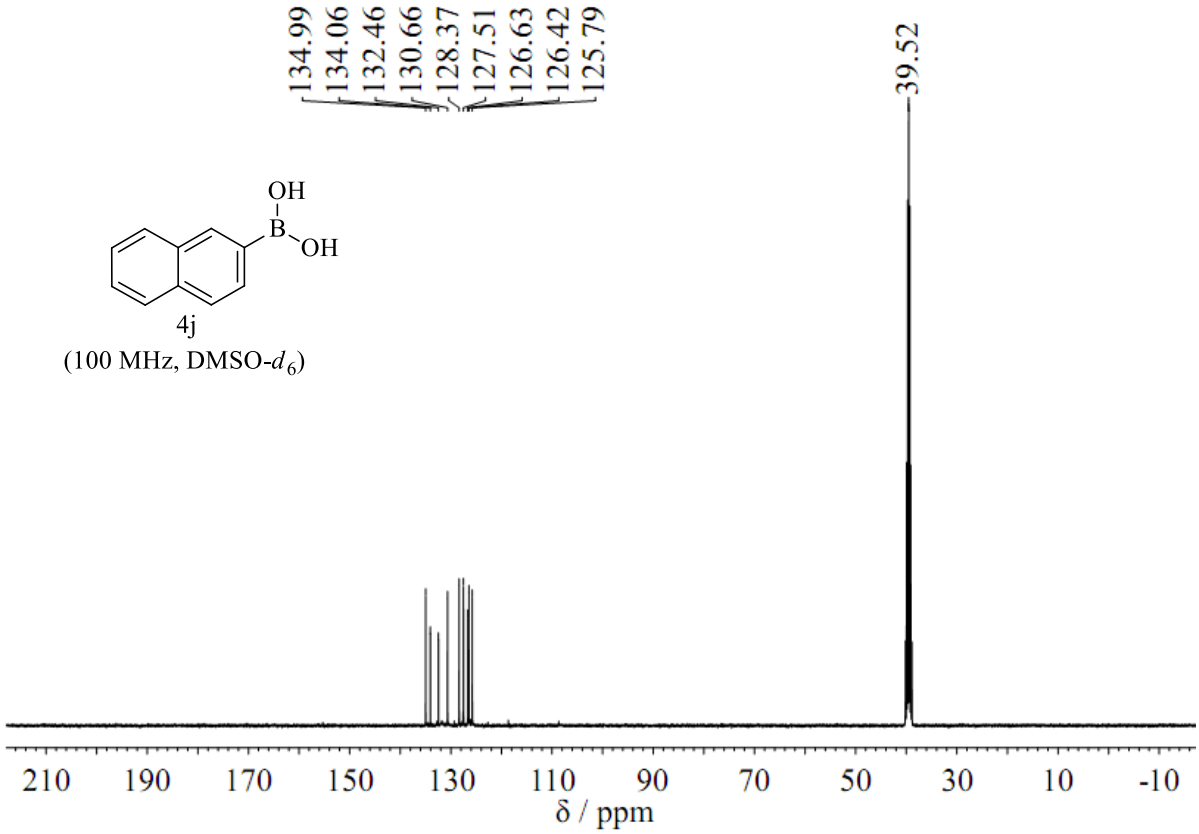

166.46
134.32
130.82
128.01
52.15
39.52
O
OH
B
H3C−O
OH
4h
(100MHz,DMSO-d6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


7.92
7.91
2.57
2.50
O
OH
B
H_3C
OH
4i
(400MHz,DMSO-d_6)
3.91
3.31
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
δ / ppm

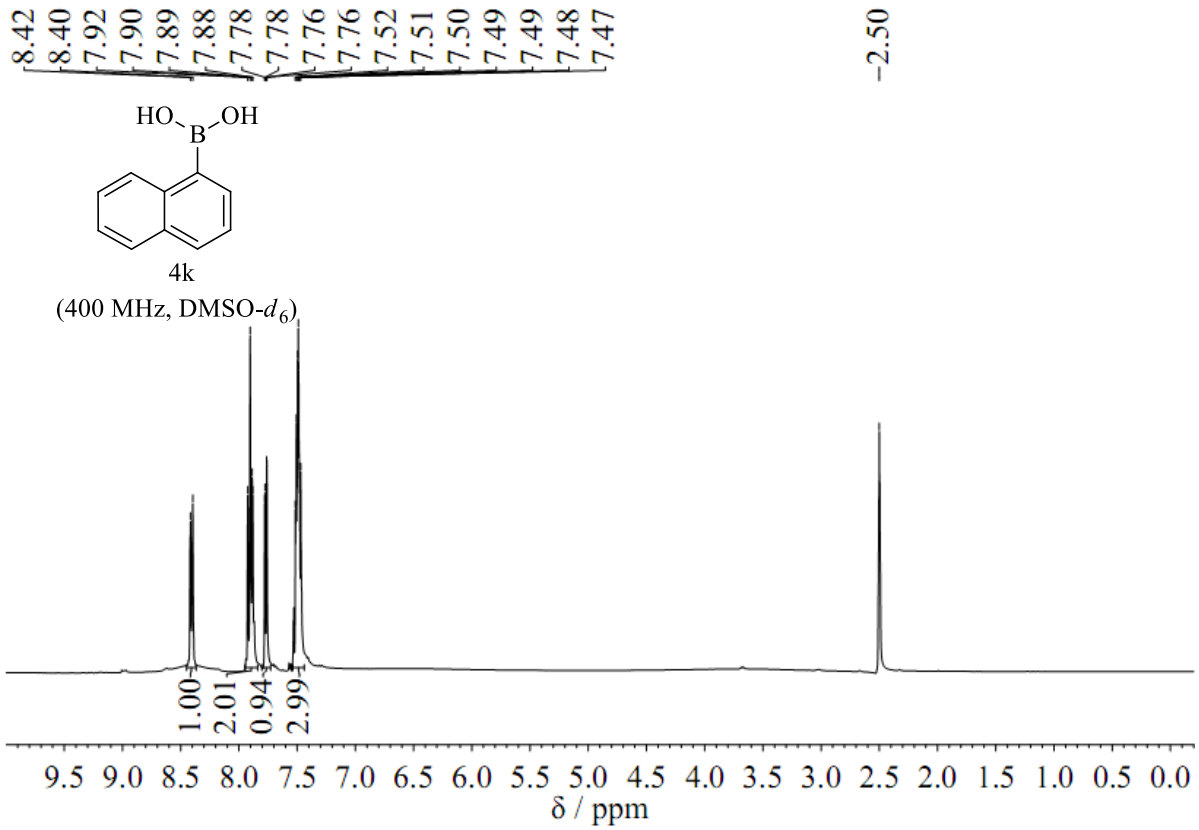

198.35
137.93
134.35
127.06
39.52
26.88
O
OH
B
H_3C
OH
4i
(100MHz,DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

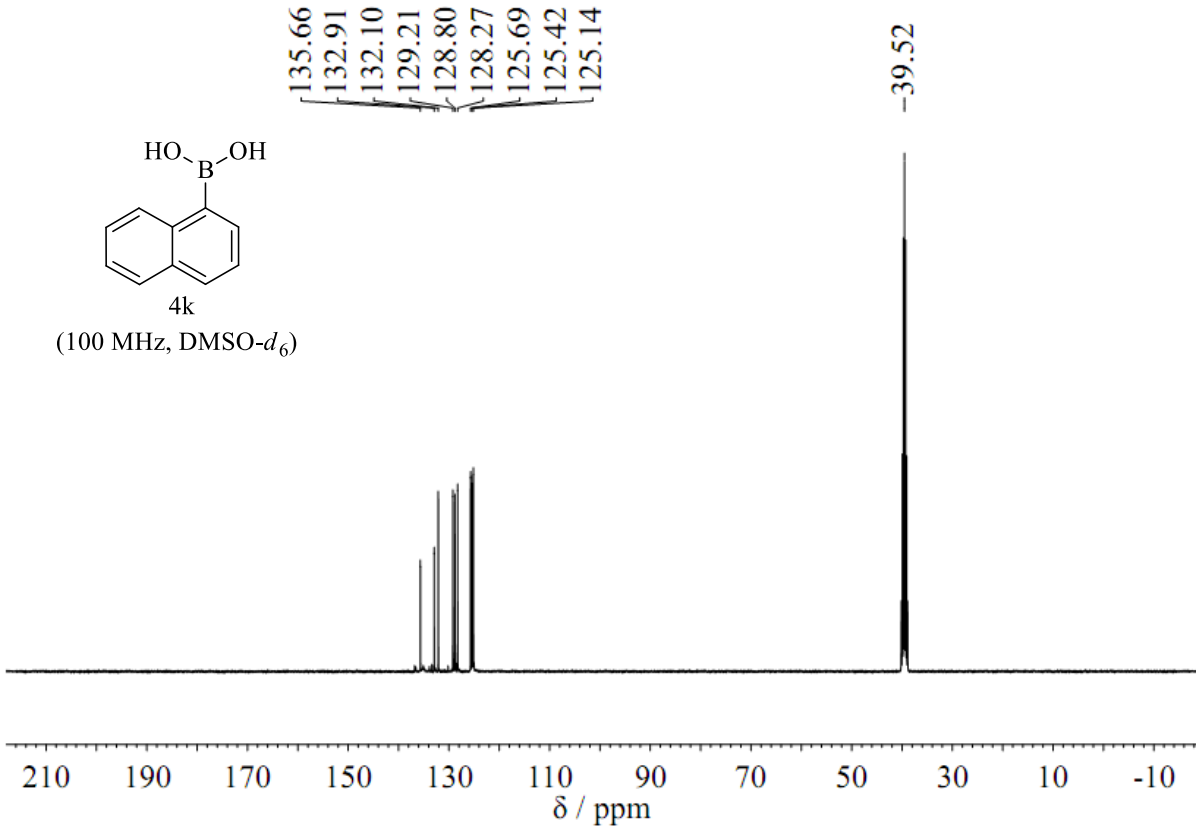


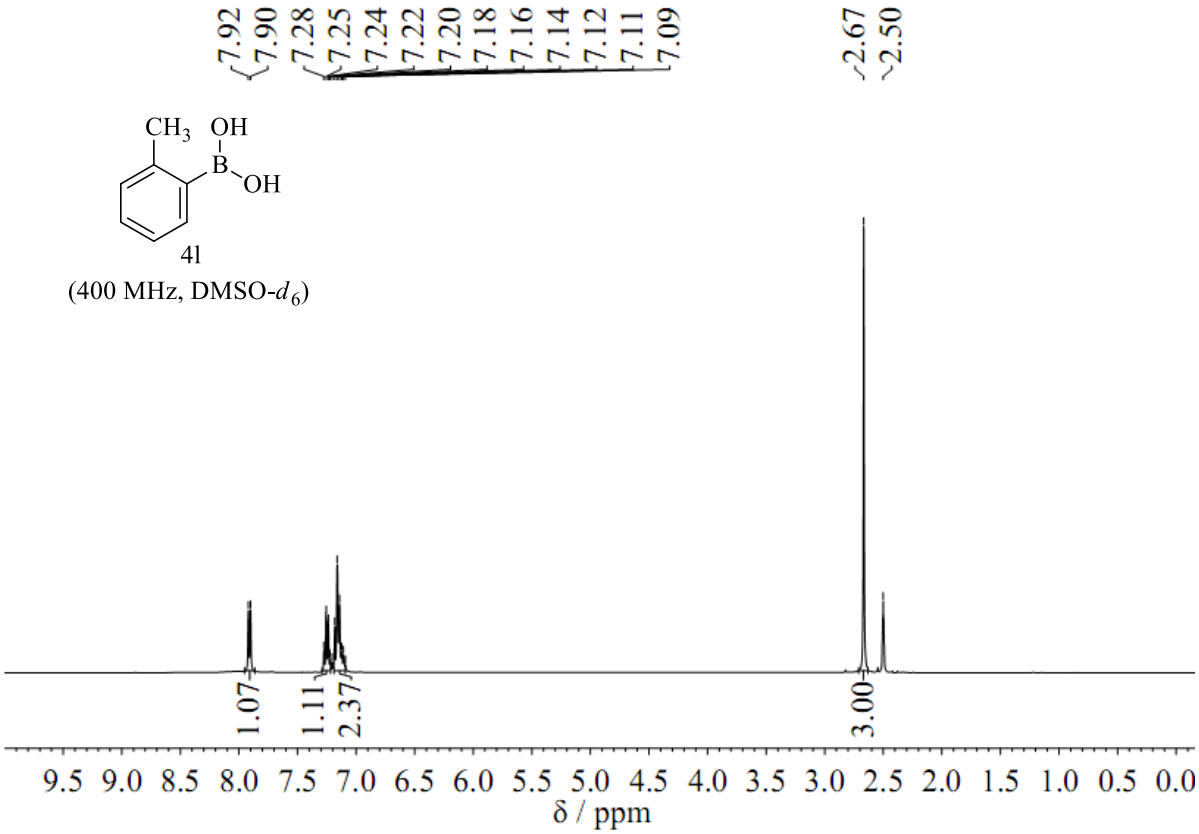
4j
(400 MHz, DMSO-d_6)



4j
(100 MHz, DMSO-d_6)

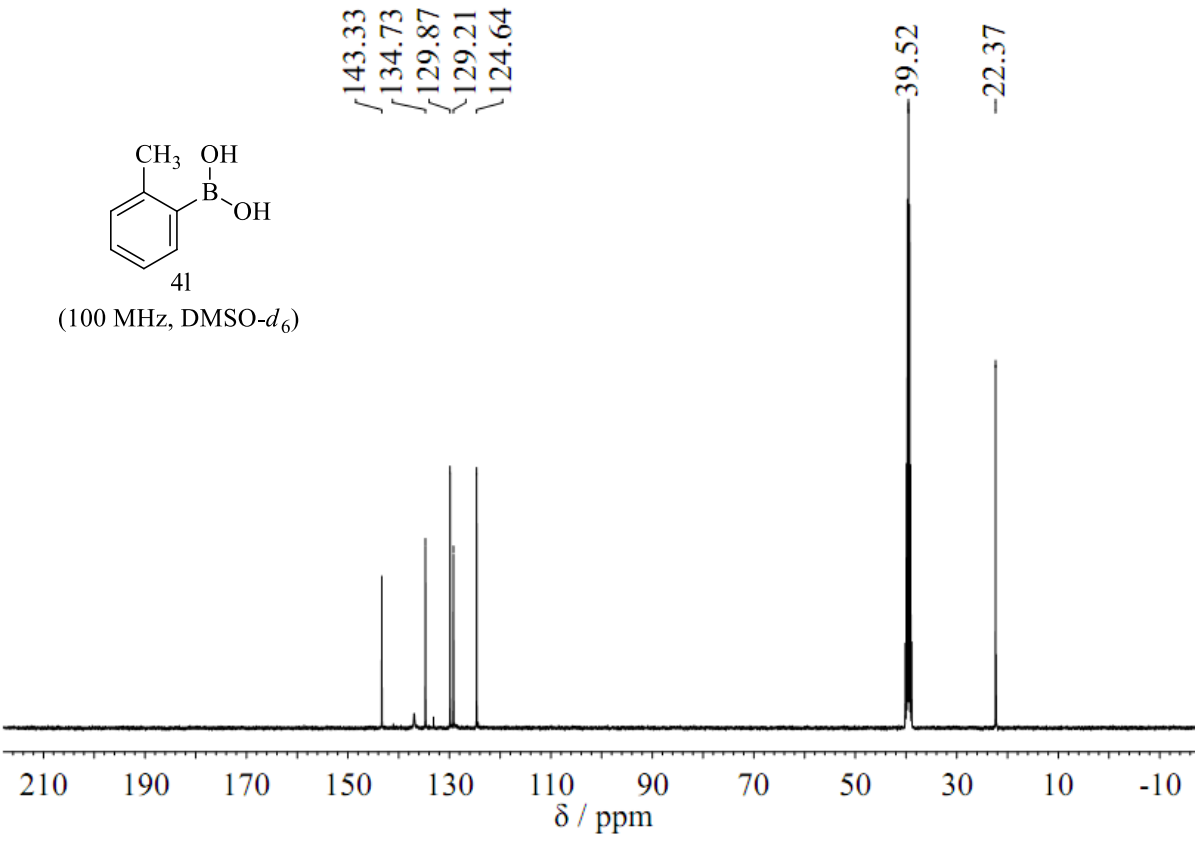

8.42
8.40
7.92
7.90
7.89
7.88
7.78
7.78
7.76
7.76
7.52
7.51
7.50
7.49
7.49
7.48
7.47
2.50
HO
B
OH
4k
(400 MHz, DMSO-d_6)
1.00
2.01
0.94
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm


135.66
132.91
132.10
129.21
128.80
128.27
125.69
125.42
125.14
39.52
HO
B
OH
4k
(100 MHz, DMSO-d_6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



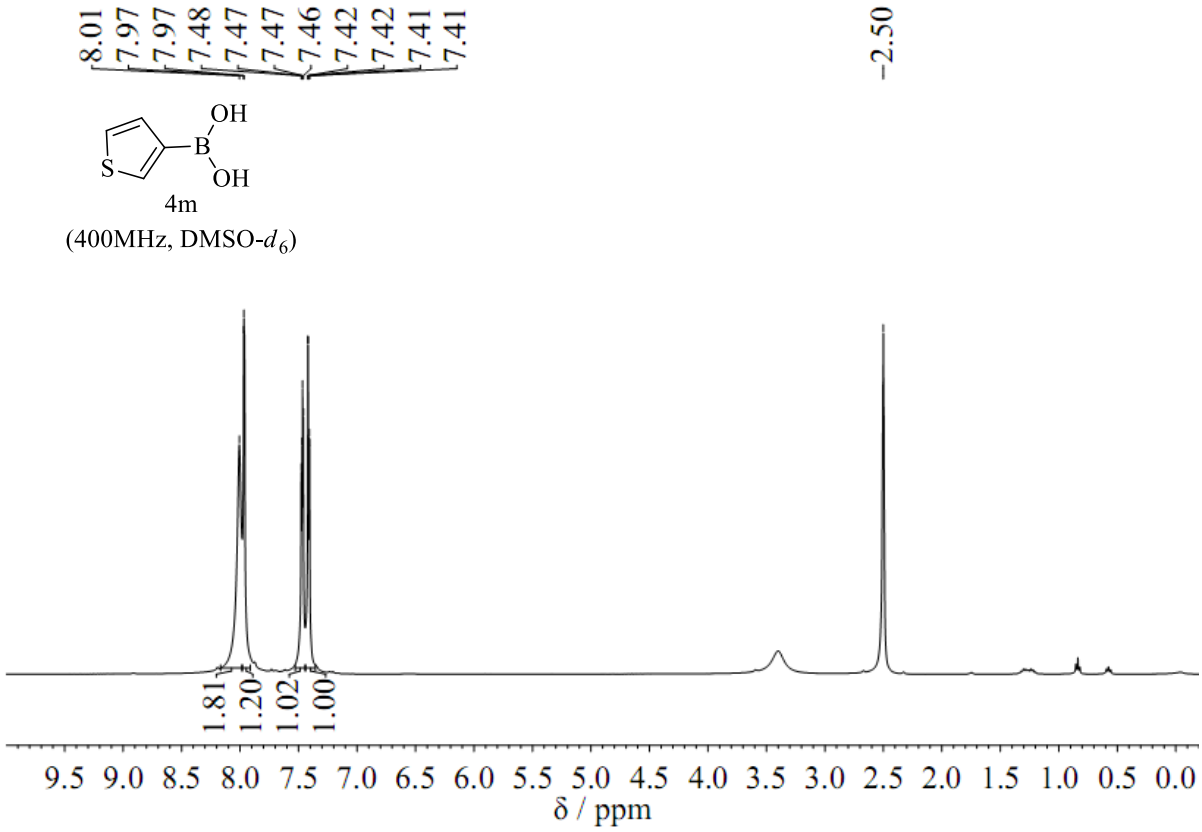
4l

(400 MHz, DMSO-d_6)



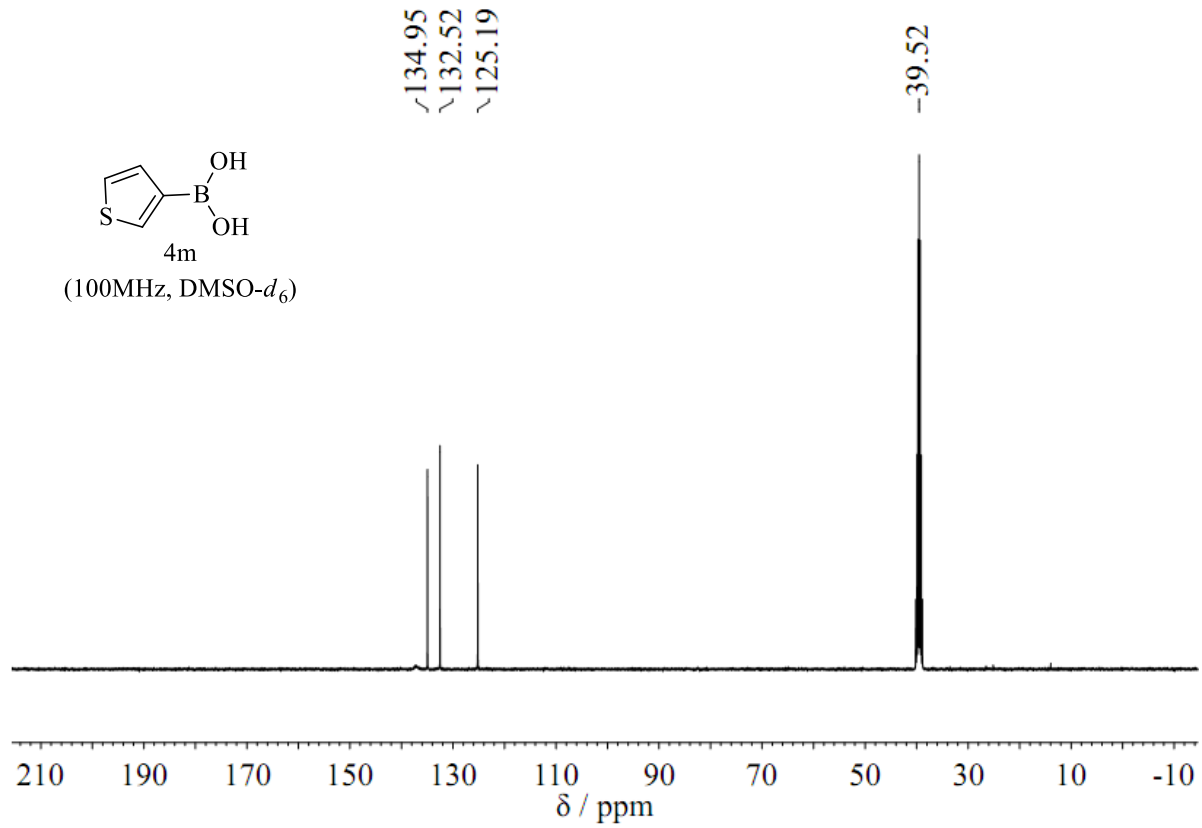
4l

(100 MHz, DMSO-d_6)



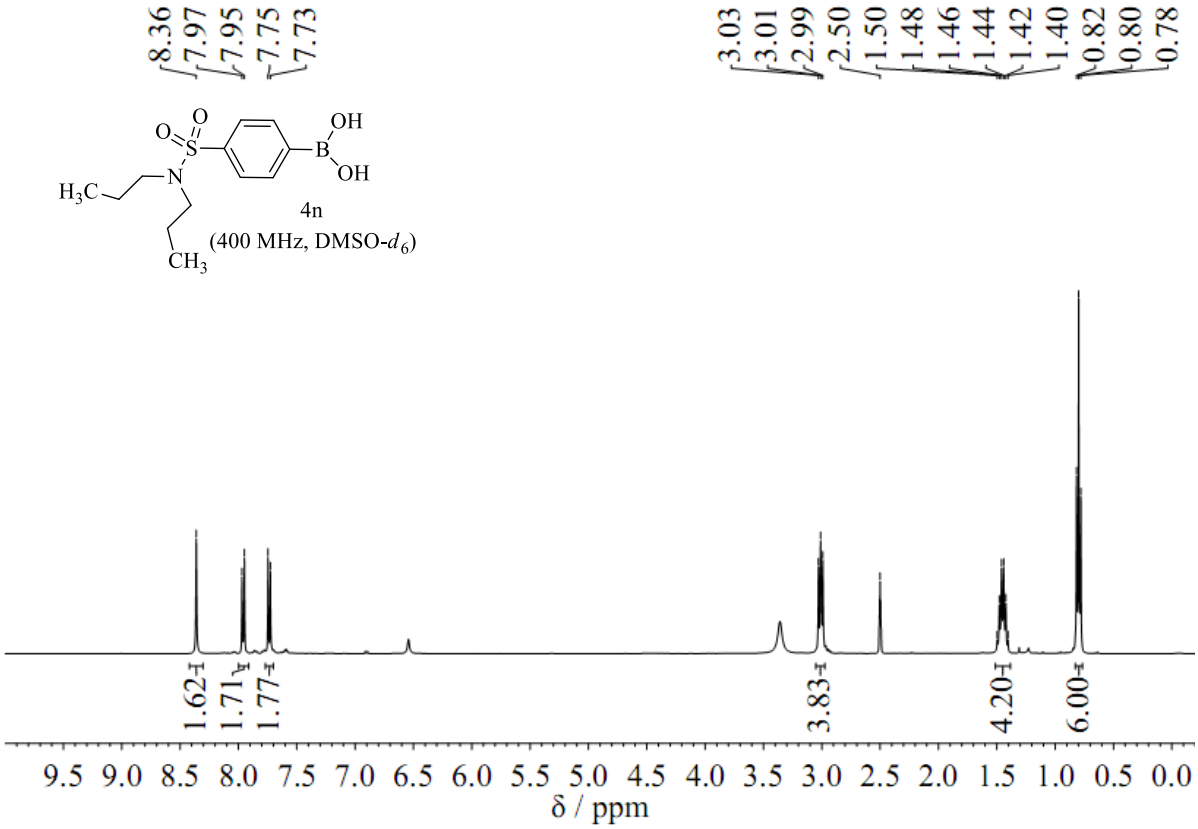
4m

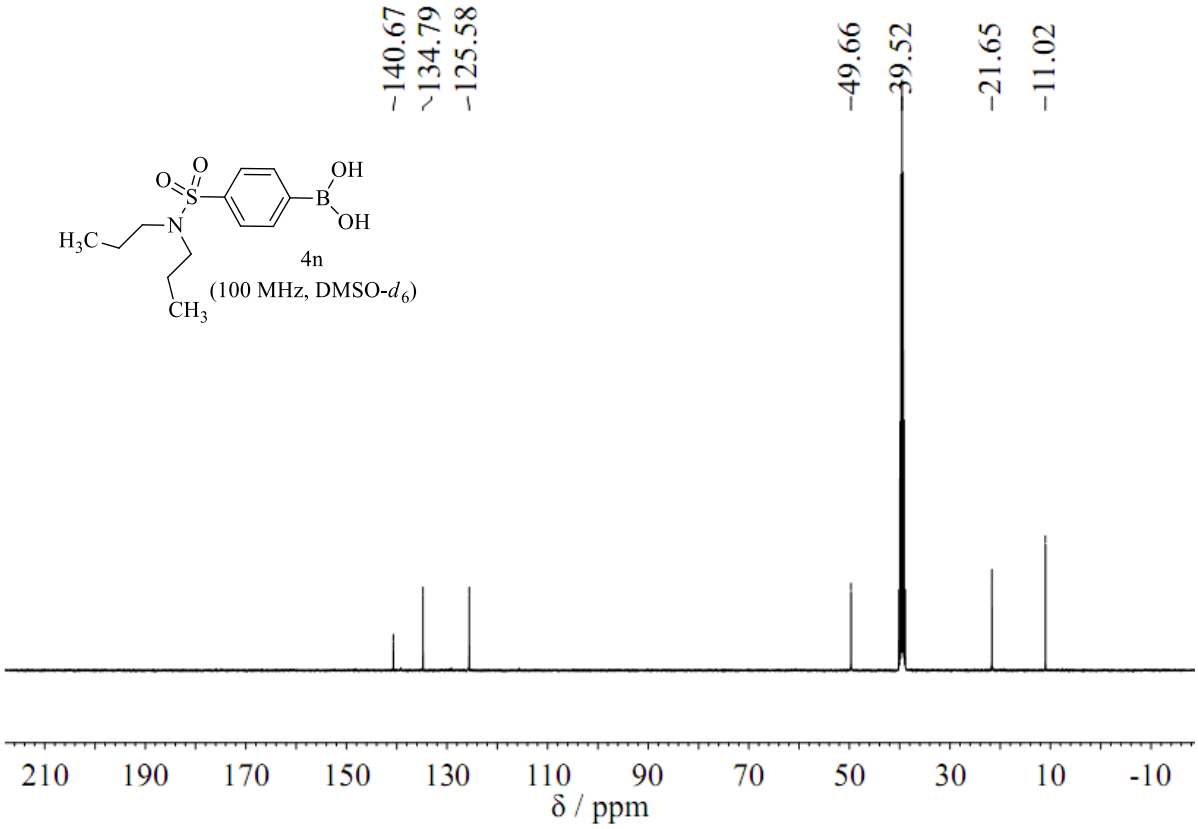
(400MHz, DMSO-d_6)

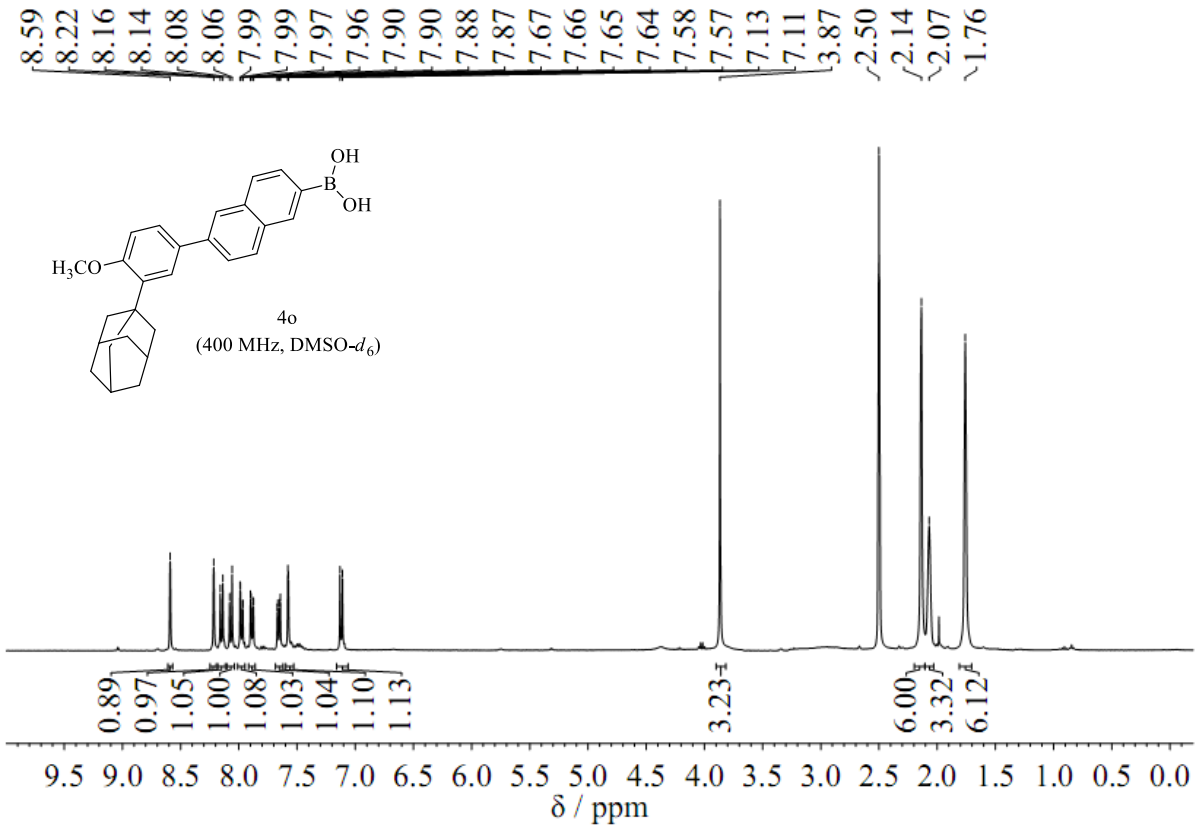


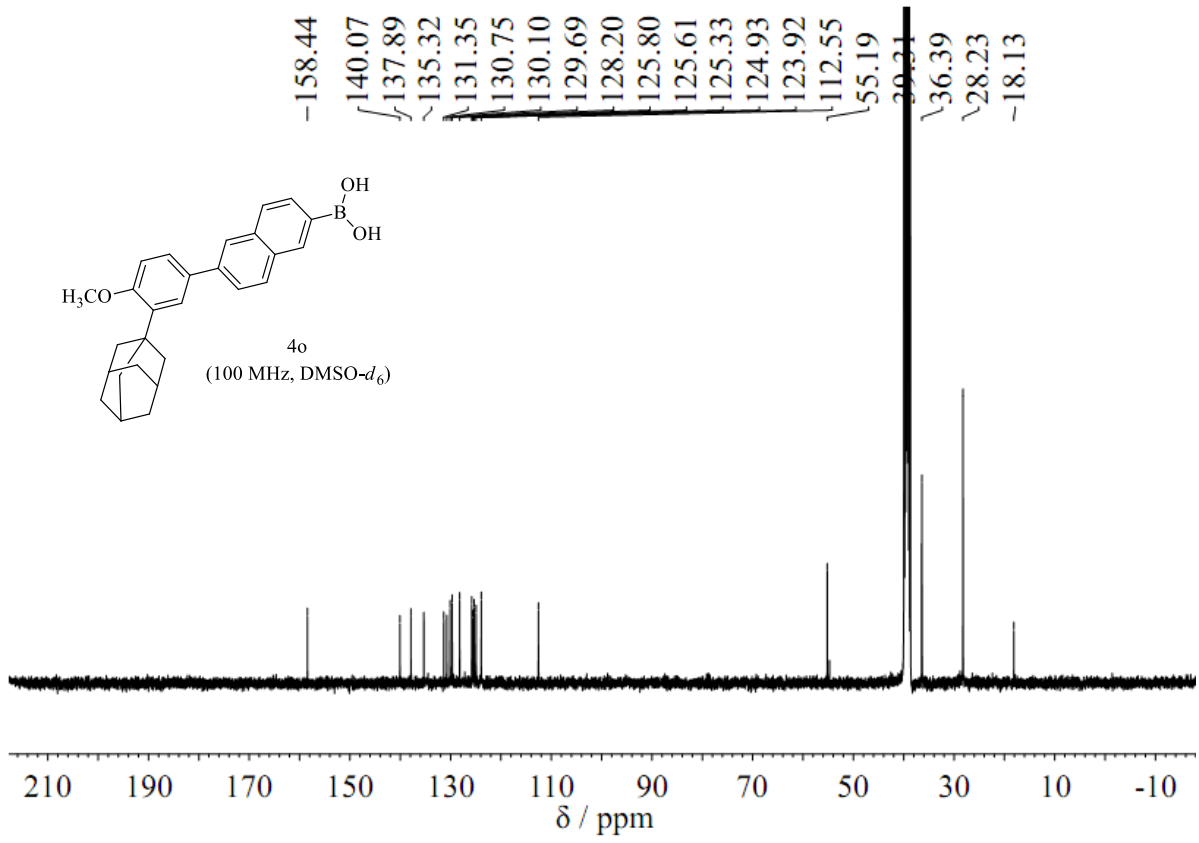
4m

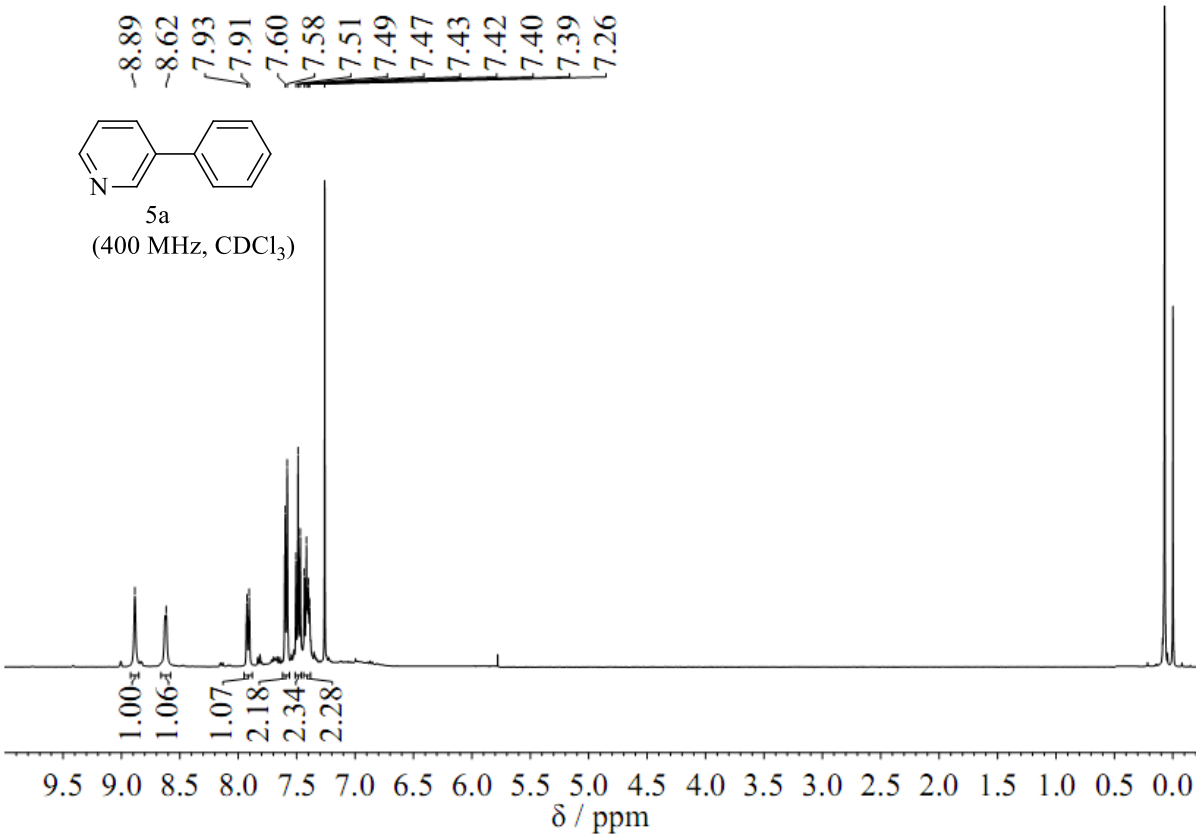
(100MHz, DMSO-d_6)

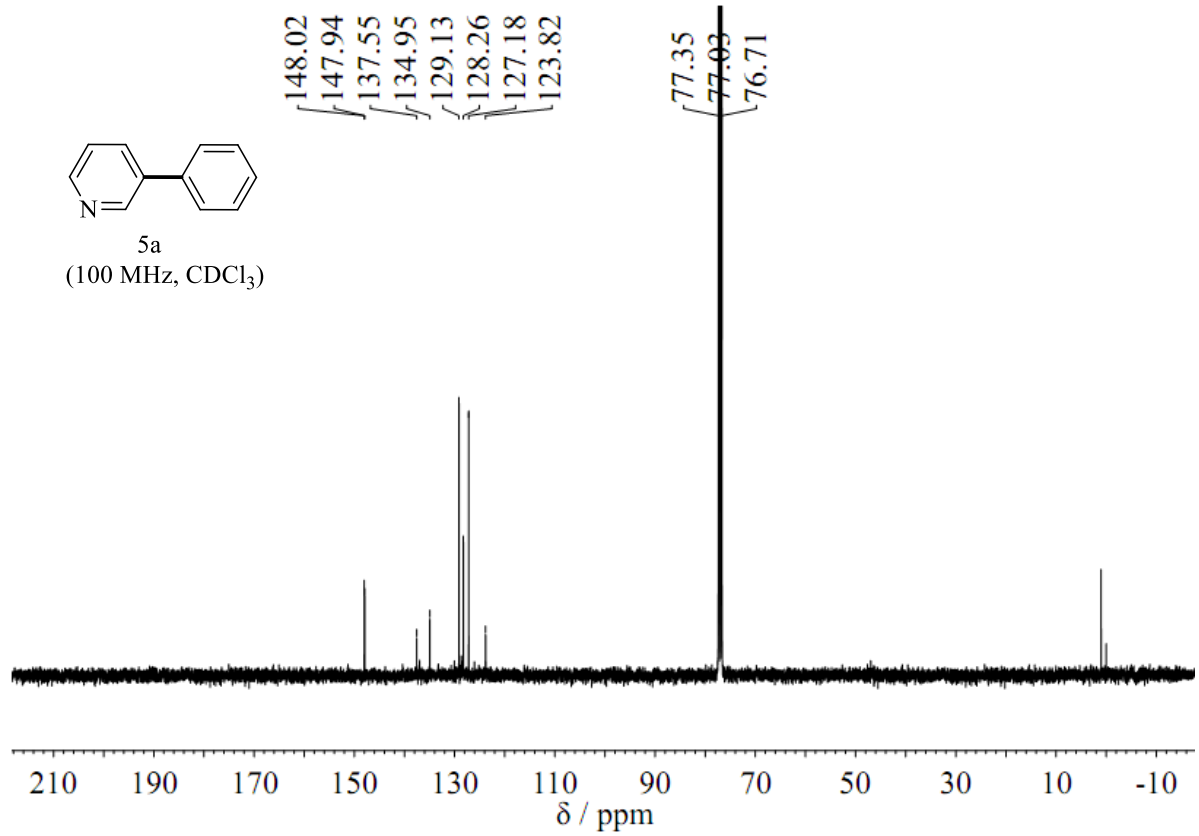

8.36
7.97
7.95
7.75
7.73
3.03
3.01
2.99
2.50
1.50
1.48
1.46
1.44
1.42
1.40
0.82
0.80
0.78
4n
(400 MHz, DMSO-d_6)
1.62
1.71
1.77
3.83
4.20
6.00
δ / ppm

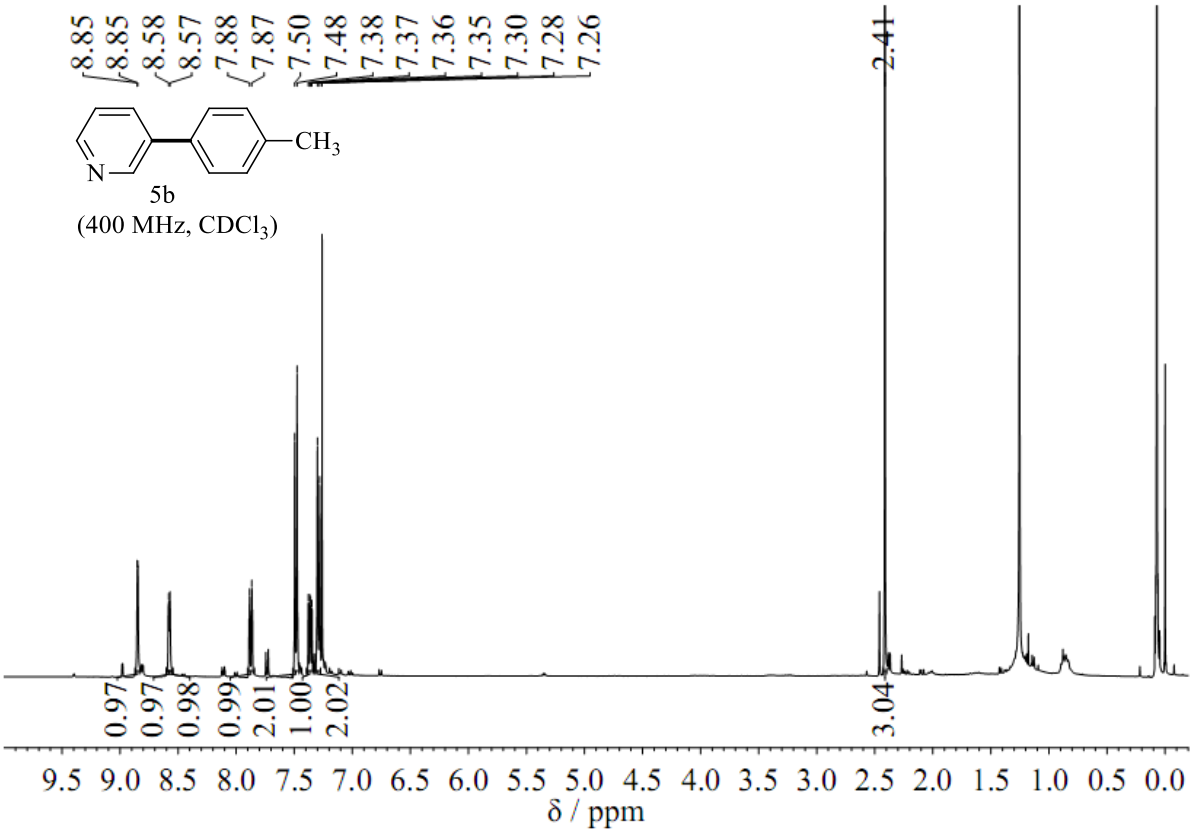

140.67
134.79
125.58
49.66
39.52
21.65
11.02
4n
(100 MHz, DMSO-d_6)
δ / ppm

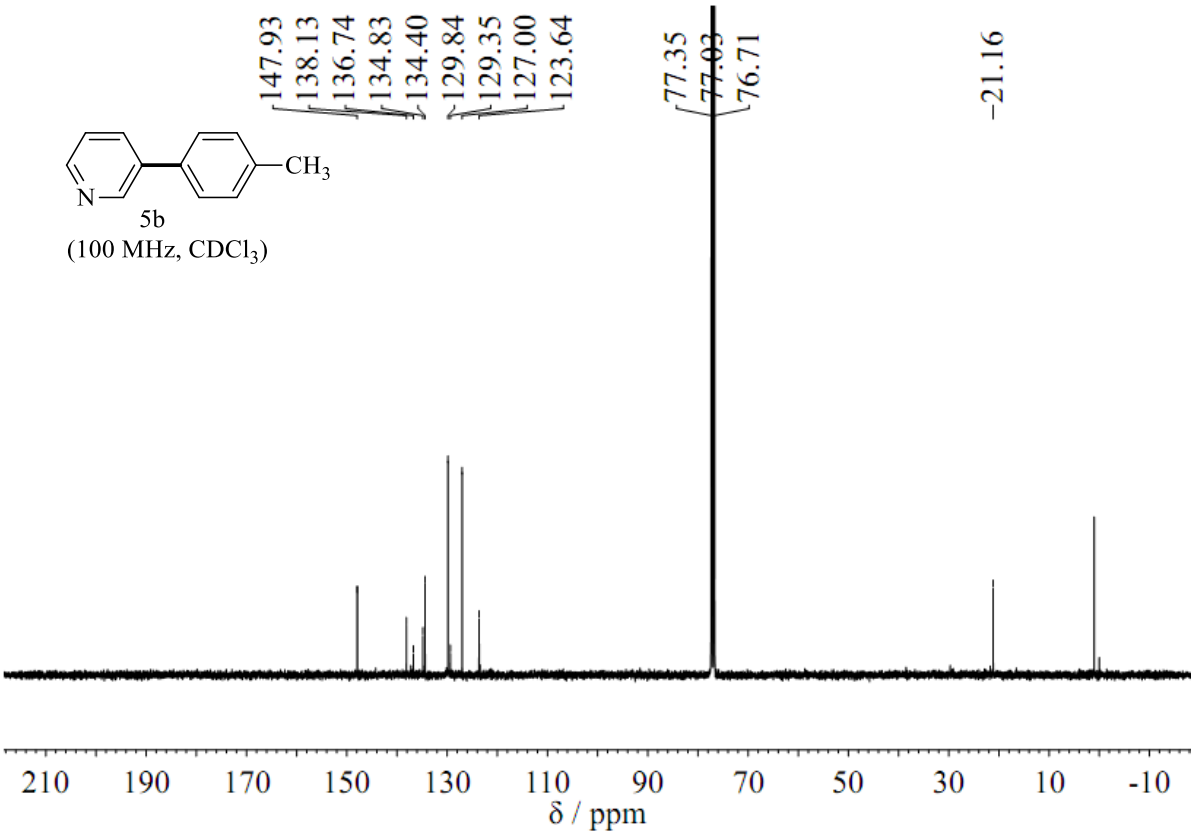

8.59
8.22
8.16
8.14
8.08
8.06
7.99
7.99
7.97
7.96
7.90
7.90
7.88
7.87
7.67
7.66
7.65
7.64
7.58
7.57
7.13
7.11
3.87
2.50
2.14
2.07
1.76
OH
B
OH
H3CO
4o
(400 MHz, DMSO-d6)
0.89
0.97
1.05
1.00
1.08
1.03
1.04
1.10
1.13
3.23
6.00
3.32
6.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

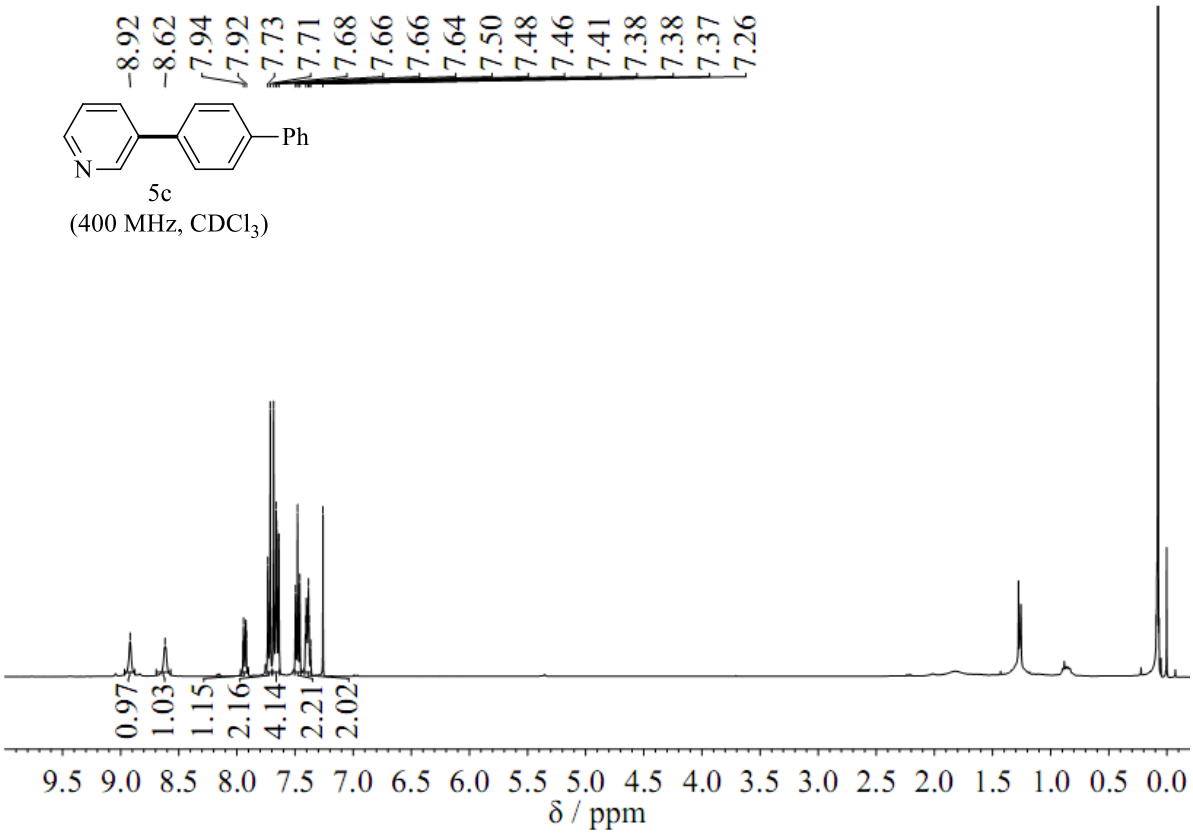

158.44
140.07
137.89
135.32
131.35
130.75
130.10
129.69
128.20
125.80
125.61
125.33
124.93
123.92
112.55
55.19
36.39
28.23
18.13
OH
B
OH
H3CO
4o
(100 MHz, DMSO-d6)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

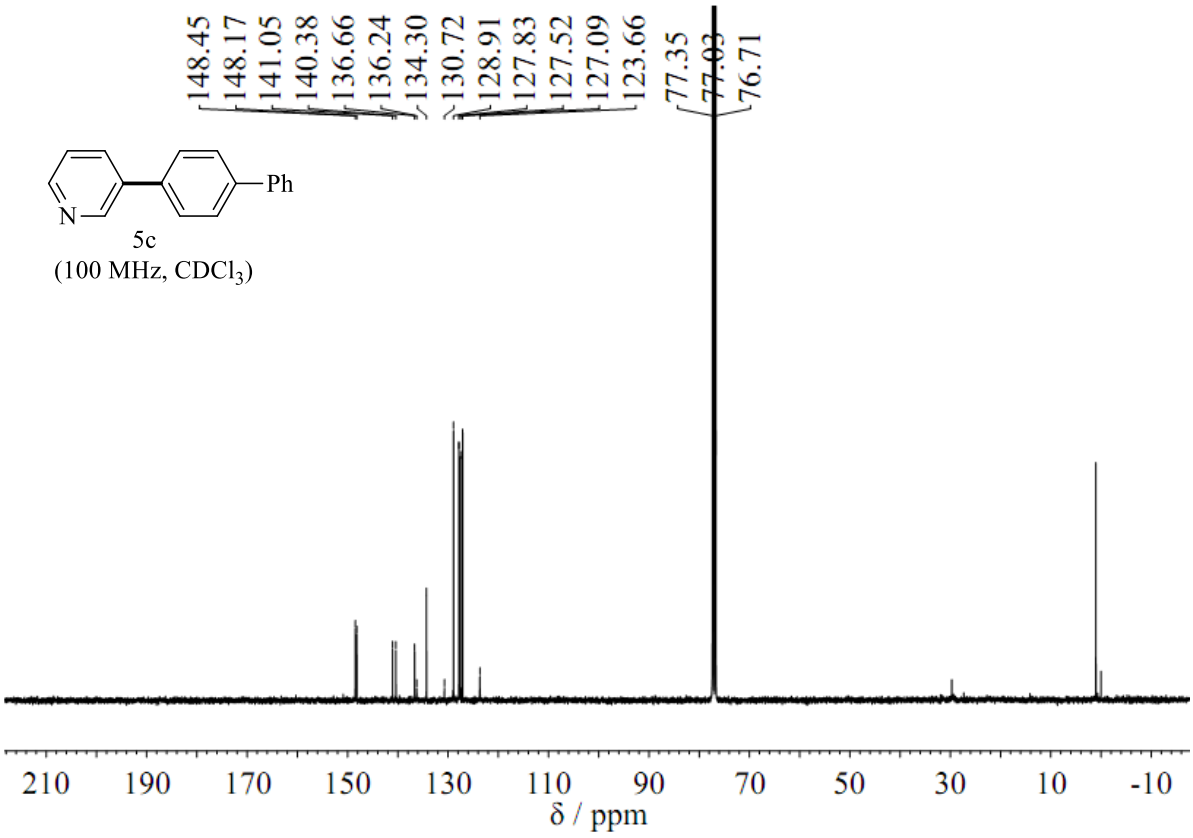

8.89
8.62
7.93
7.91
7.60
7.58
7.51
7.49
7.47
7.43
7.42
7.40
7.39
7.26
N
5a
(400 MHz, CDCl3)
1.00
1.06
1.07
2.18
2.34
2.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

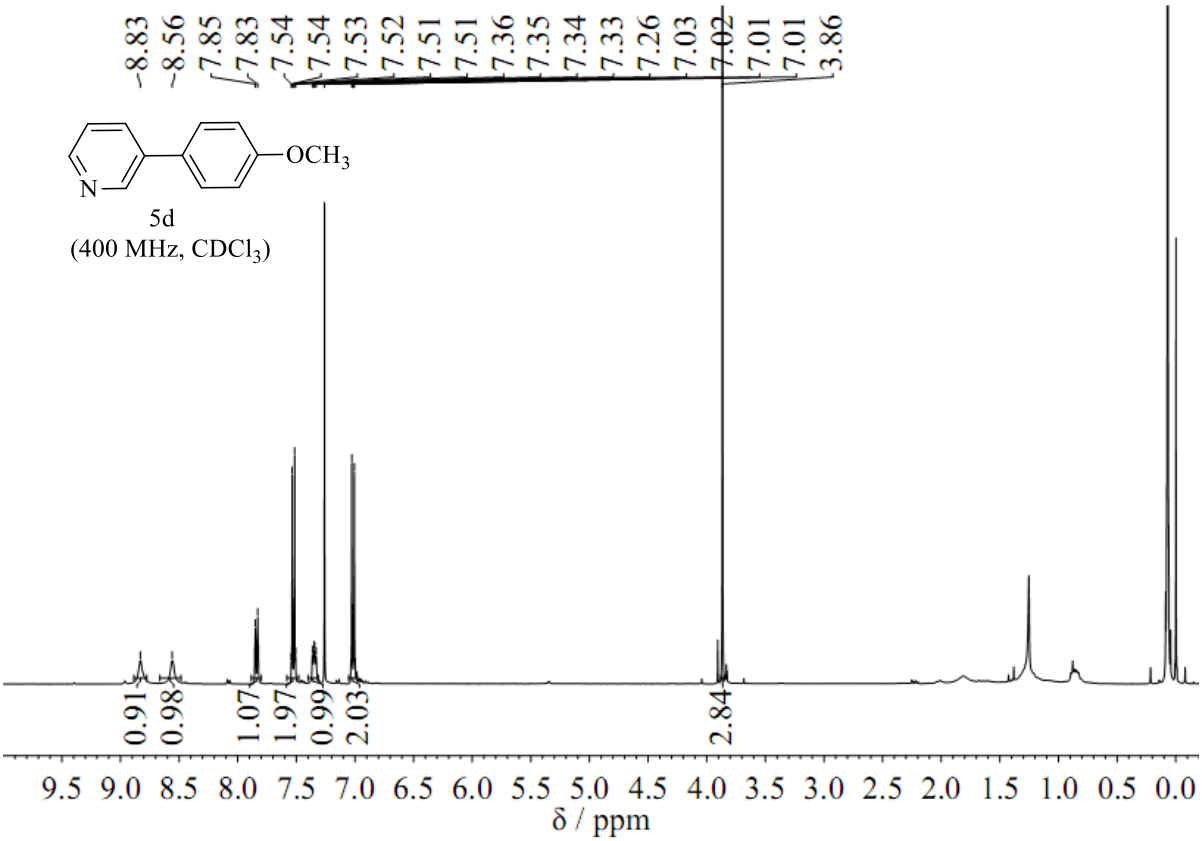

148.02
147.94
137.55
134.95
129.13
128.26
127.18
123.82
77.35
77.03
76.71
N
5a
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

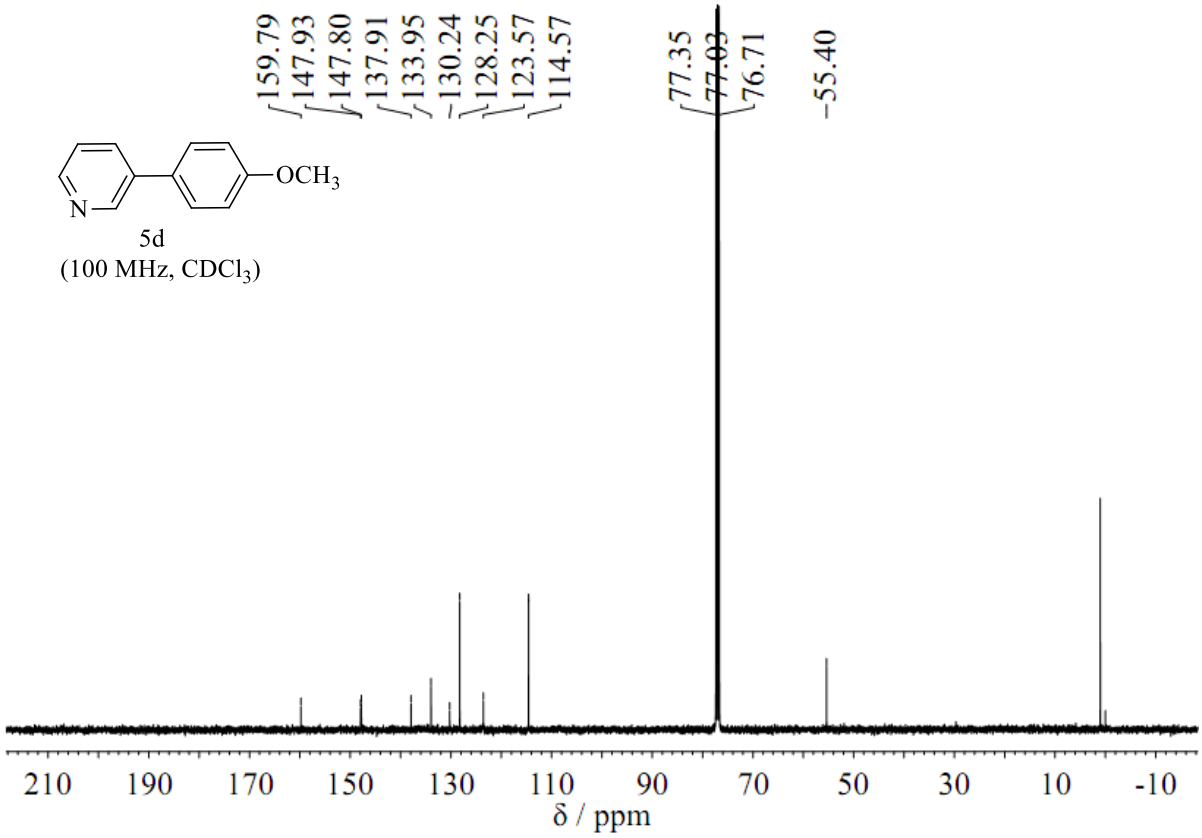

8.85
8.85
8.58
8.57
7.88
7.87
7.50
7.48
7.38
7.37
7.36
7.35
7.30
7.28
7.26
2.41
CH3
N
5b
(400 MHz, CDCl3)
0.97
0.97
0.98
0.99
2.01
1.00
2.02
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

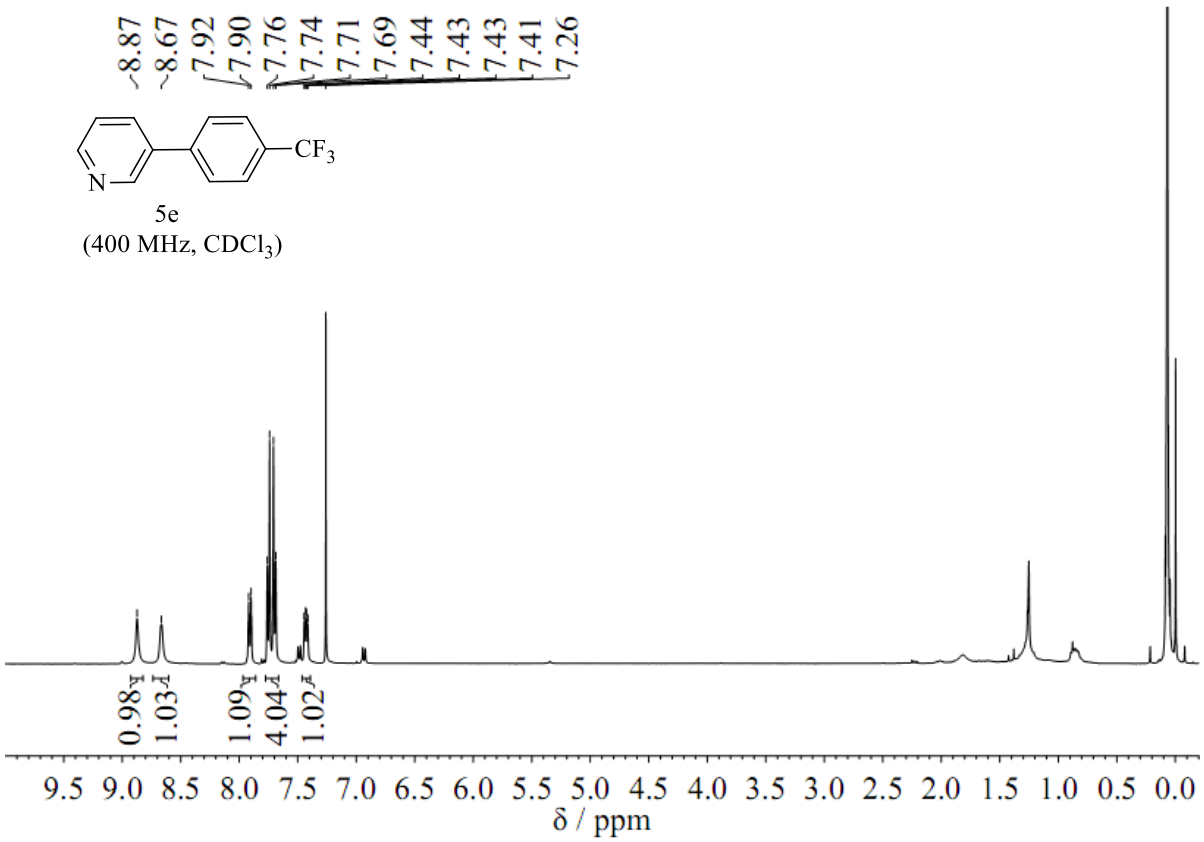

147.93
138.13
136.74
134.83
134.40
129.84
129.35
127.00
123.64
77.35
77.03
76.71
21.16
CH3
N
5b
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.92
8.62
7.94
7.92
7.73
7.71
7.68
7.66
7.66
7.64
7.50
7.48
7.46
7.41
7.38
7.38
7.37
7.26
Ph
N
5c
(400 MHz, CDCl3)
0.97
1.03
1.15
2.16
4.14
2.21
2.02
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
δ / ppm

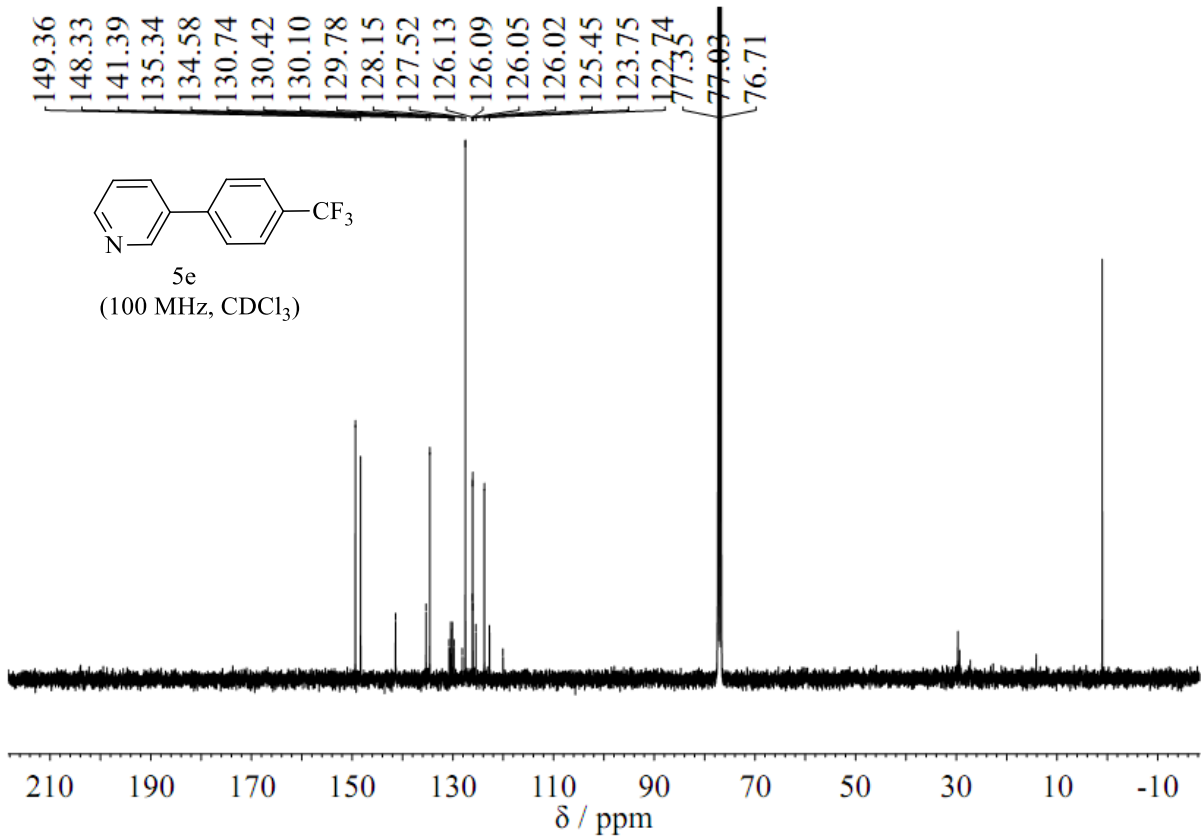

148.45
148.17
141.05
140.38
136.66
136.24
134.30
130.72
128.91
127.83
127.52
127.09
123.66
77.35
77.03
76.71
Ph
N
5c
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.83
8.56
7.85
7.83
7.54
7.54
7.53
7.52
7.51
7.51
7.36
7.35
7.34
7.33
7.26
7.03
7.02
7.01
7.01
3.86
OCH3
N
5d
(400 MHz, CDCl3)
0.91
0.98
1.07
1.97
0.99
2.03
2.84
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
δ / ppm

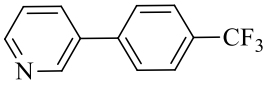

159.79
147.93
147.80
137.91
133.95
130.24
128.25
123.57
114.57
77.35
77.03
76.71
55.40
OCH3
N
5d
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



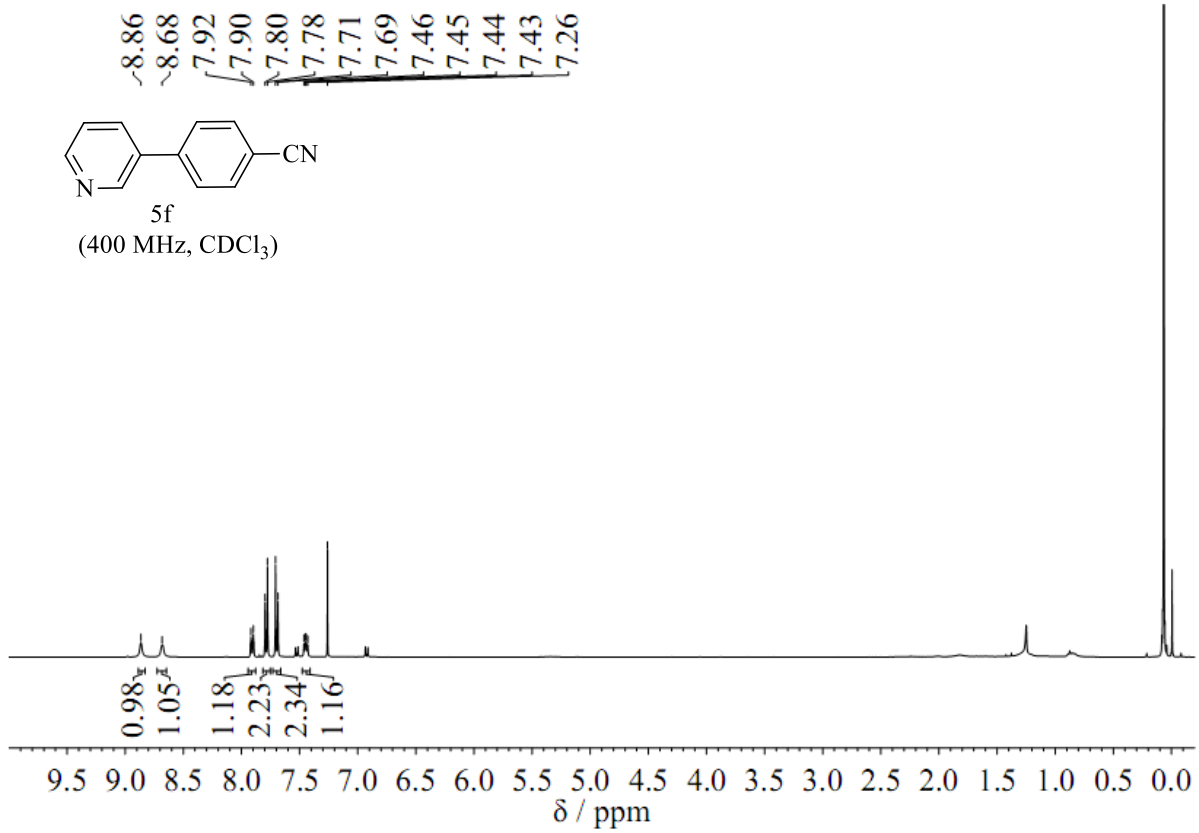
5e
(400 MHz, $CDCl_3$)



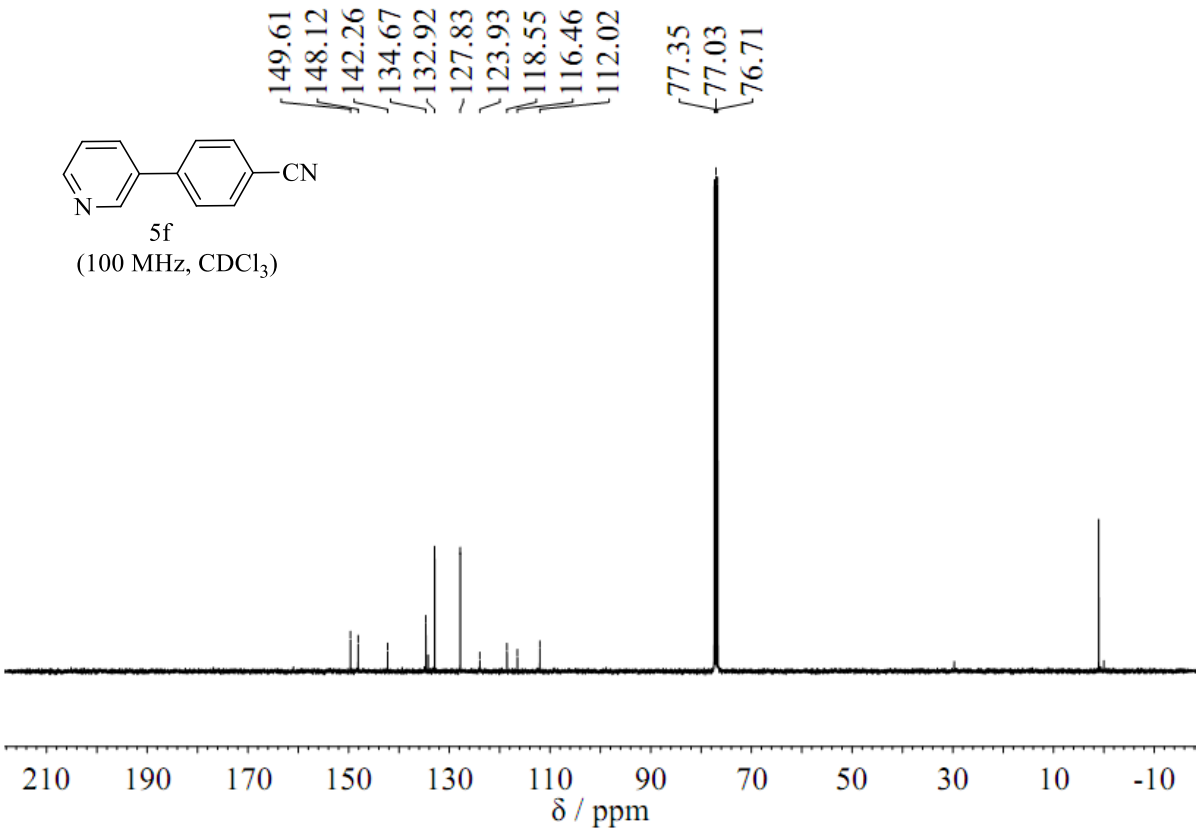
5e
(100 MHz, $CDCl_3$)



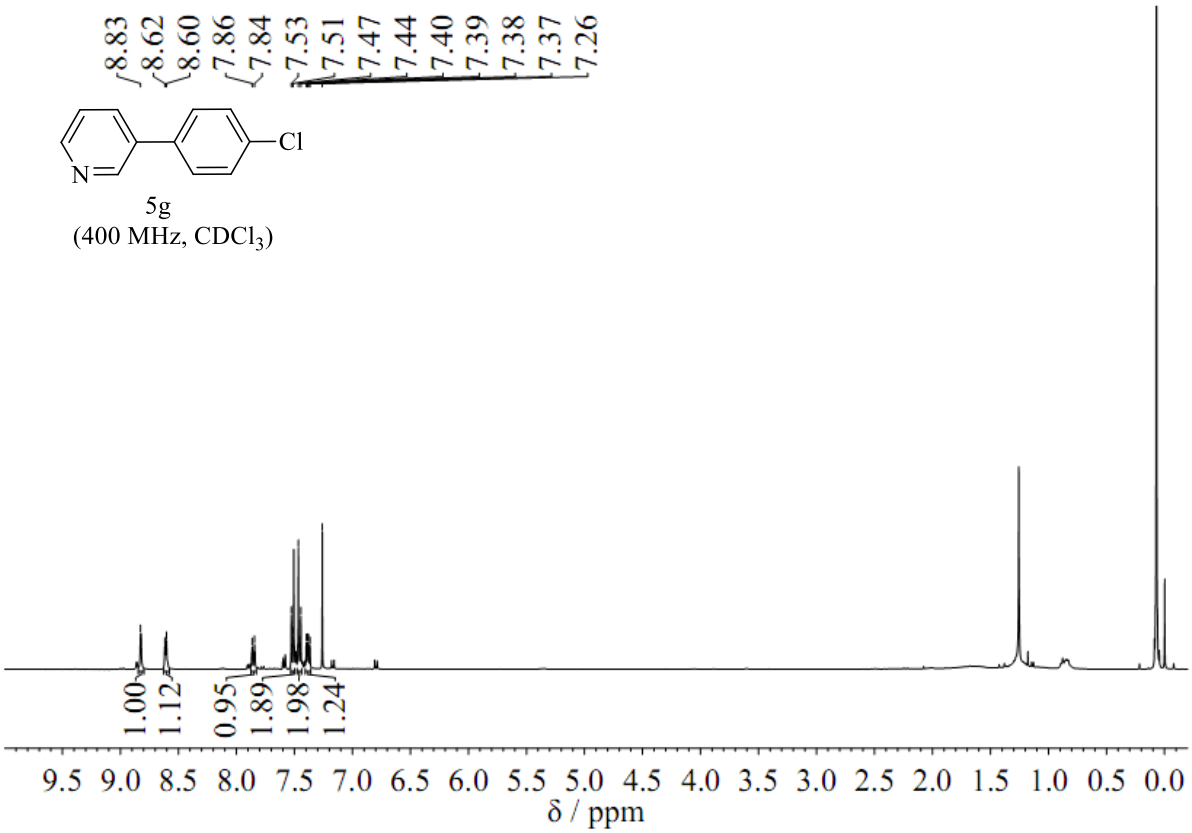
5e
(376 MHz, $CDCl_3$)



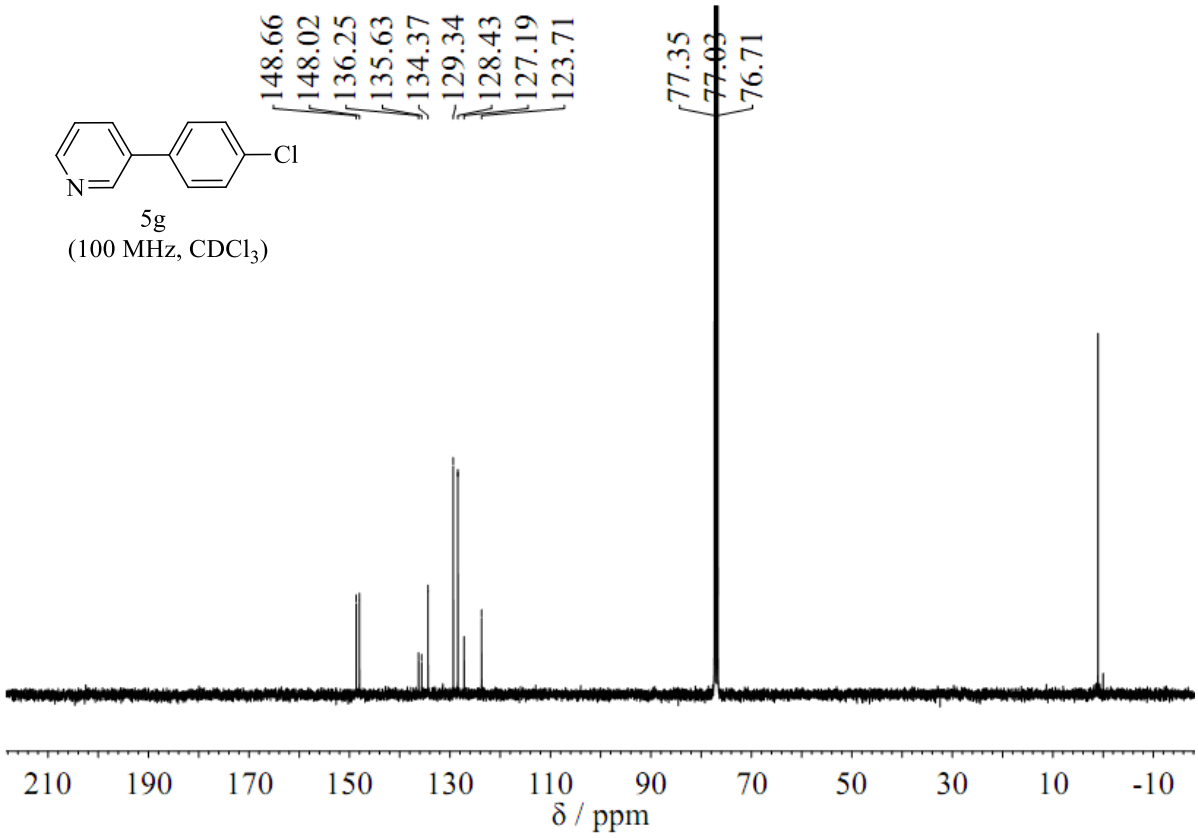
5f
(400 MHz, $CDCl_3$)



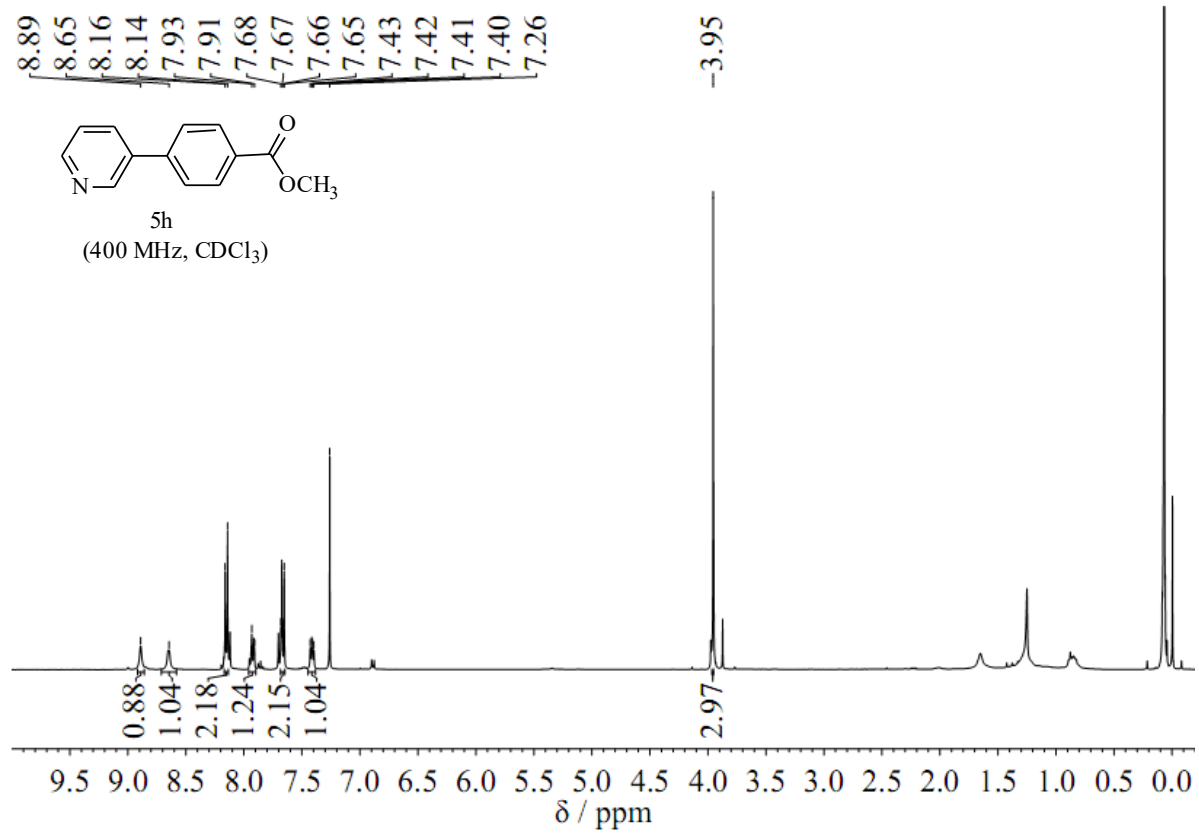
5f
(100 MHz, $CDCl_3$)



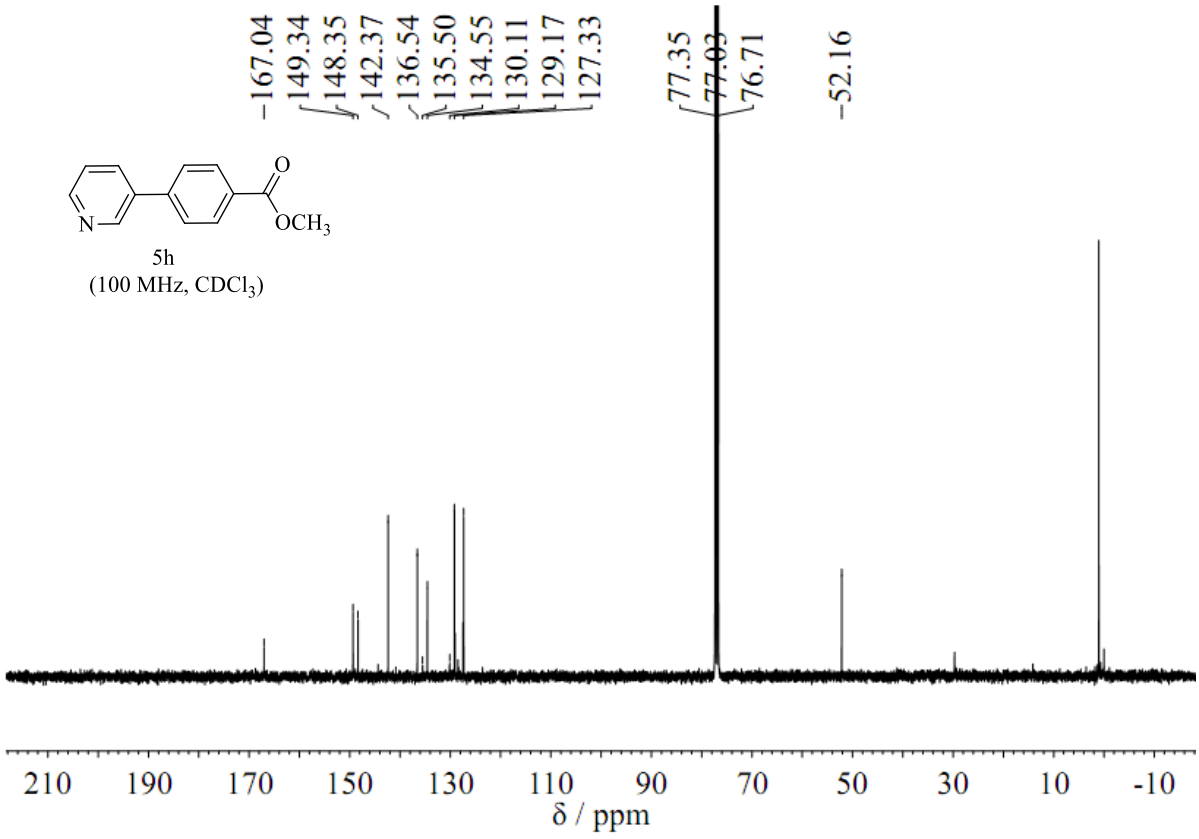
5g
(400 MHz, $CDCl_3$)



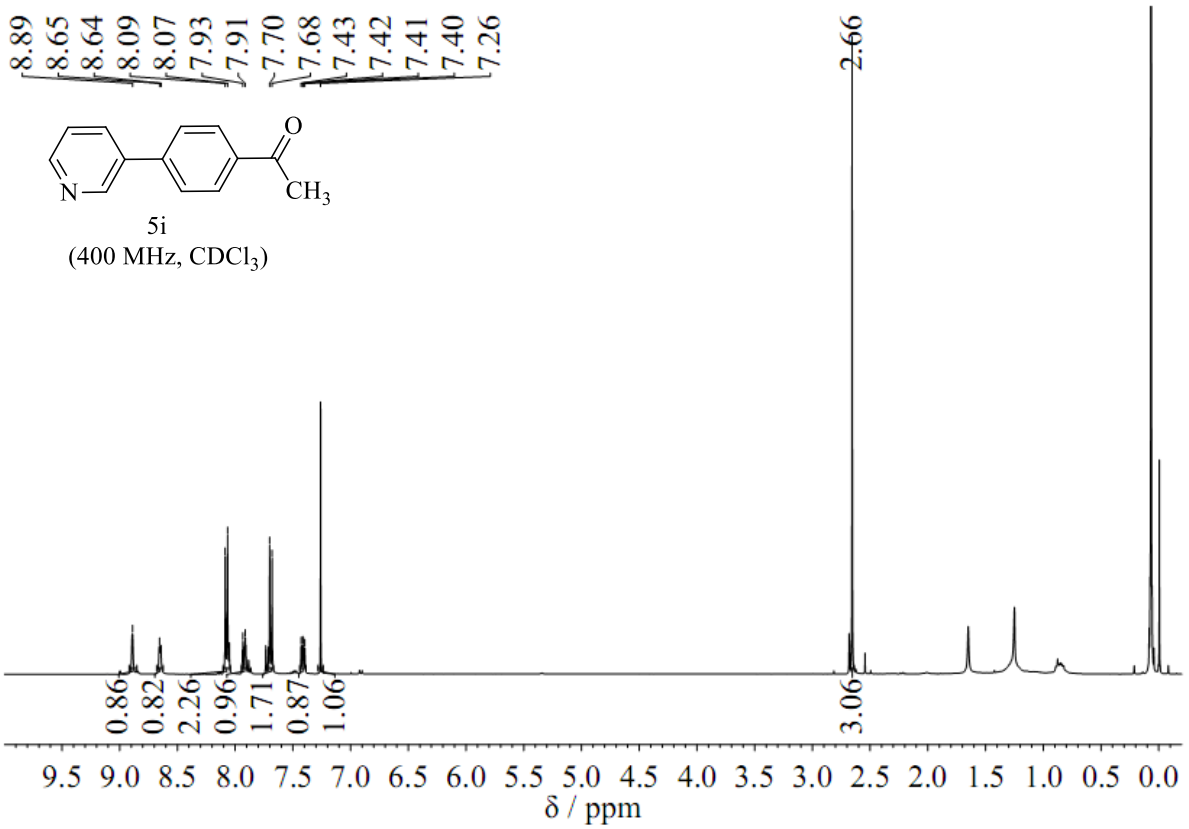
5g
(100 MHz, $CDCl_3$)



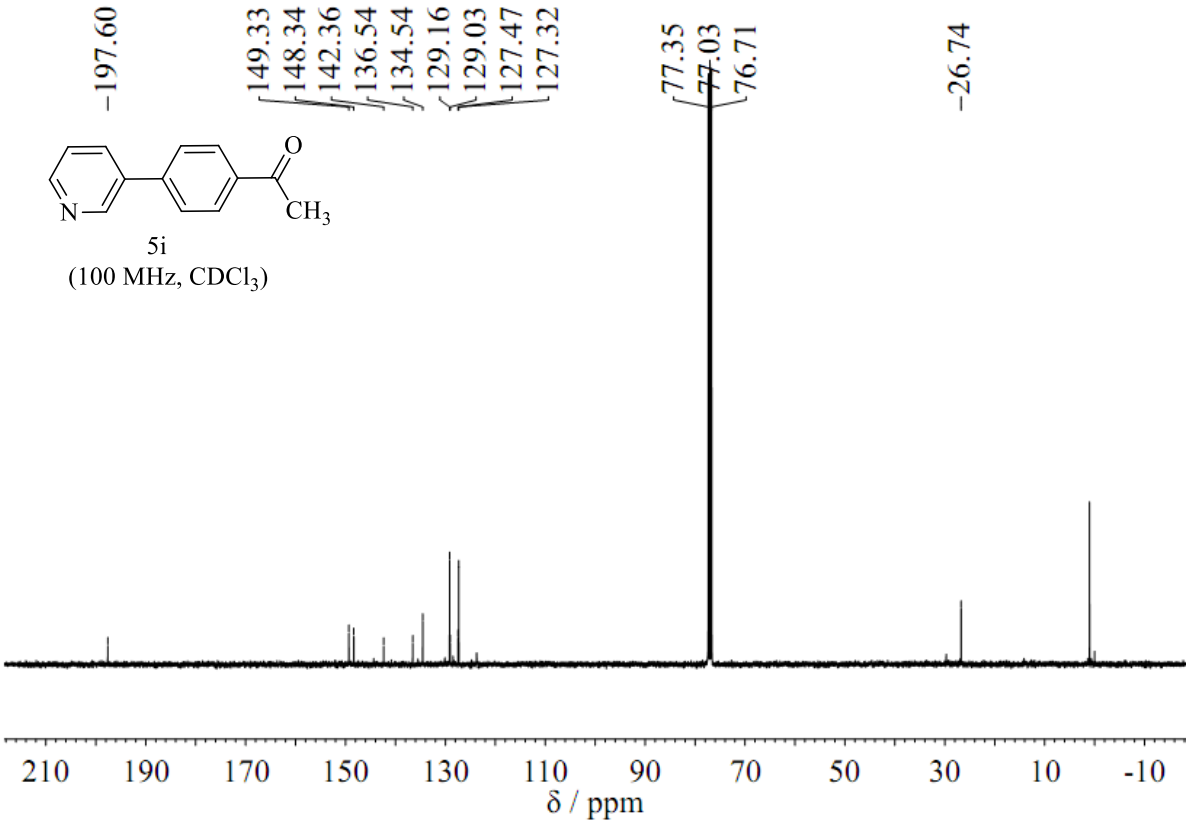
5h
(400 MHz, $CDCl_3$)



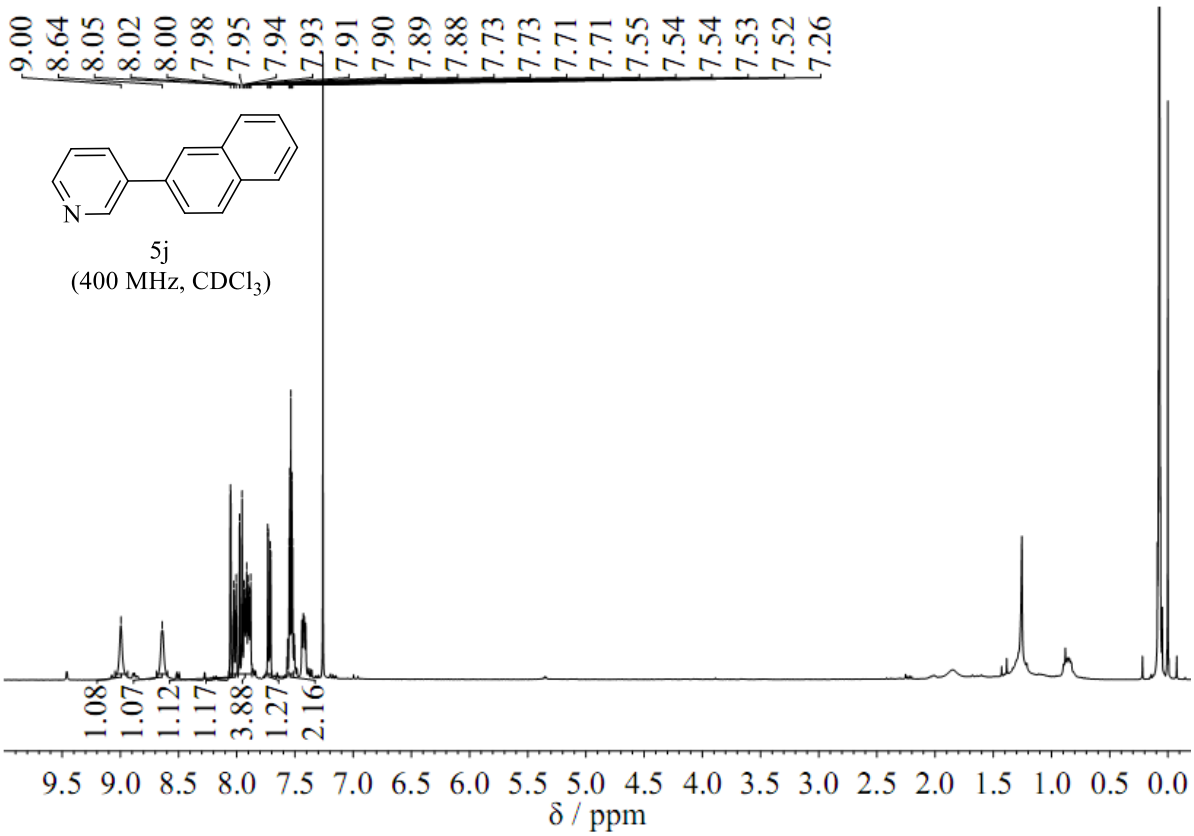
5h
(100 MHz, $CDCl_3$)



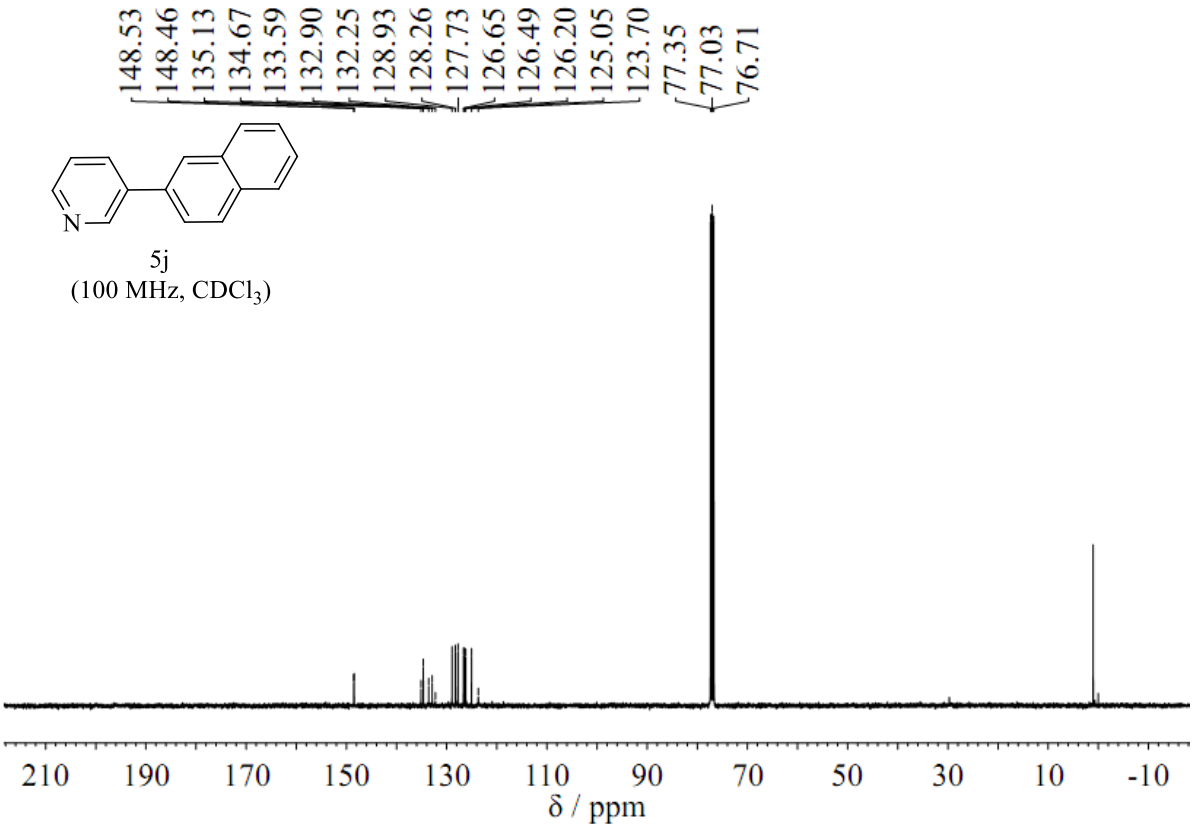
5i
(400 MHz, $CDCl_3$)



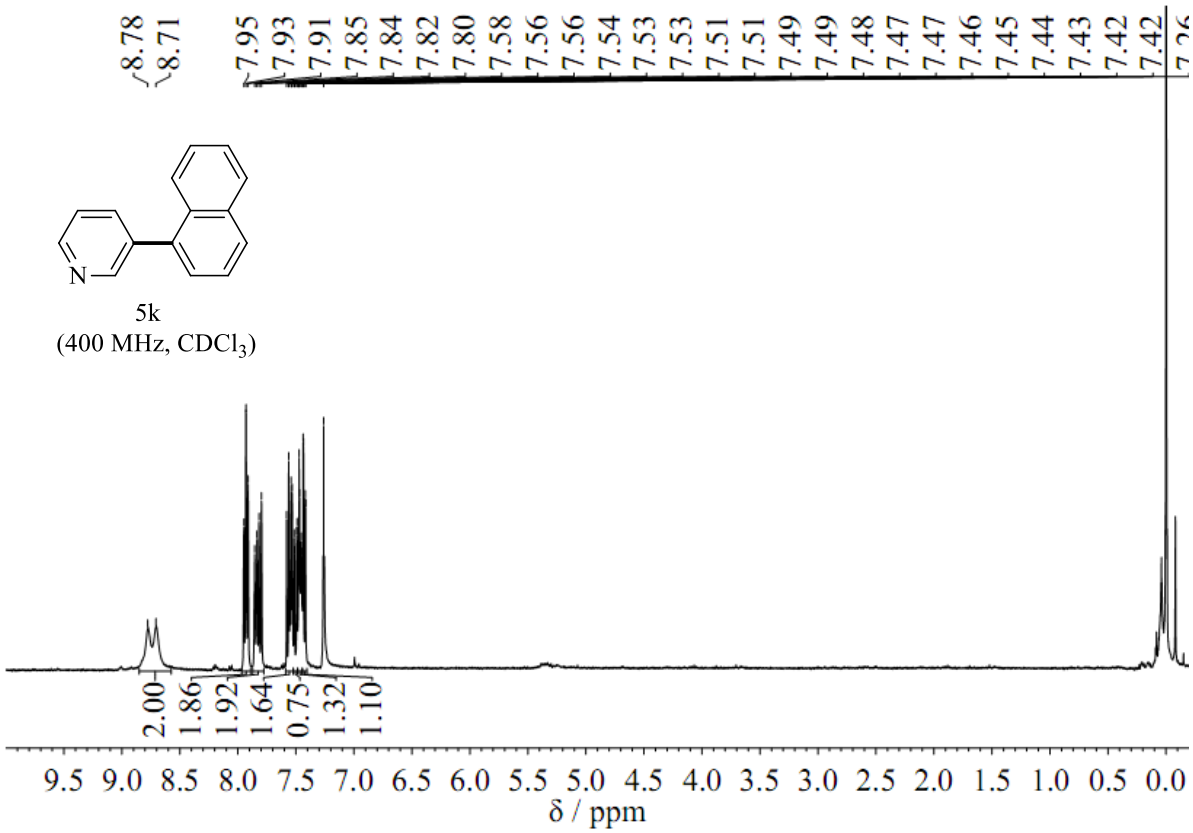
5i
(100 MHz, $CDCl_3$)

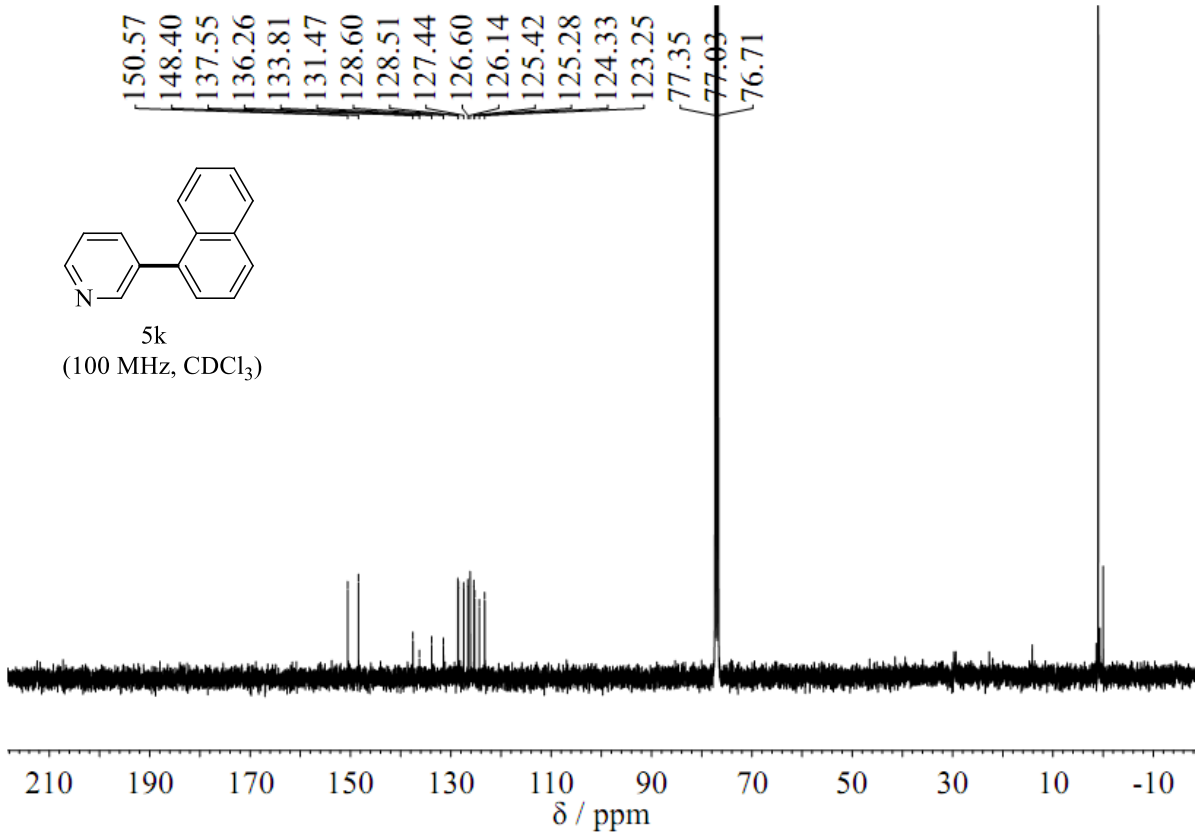


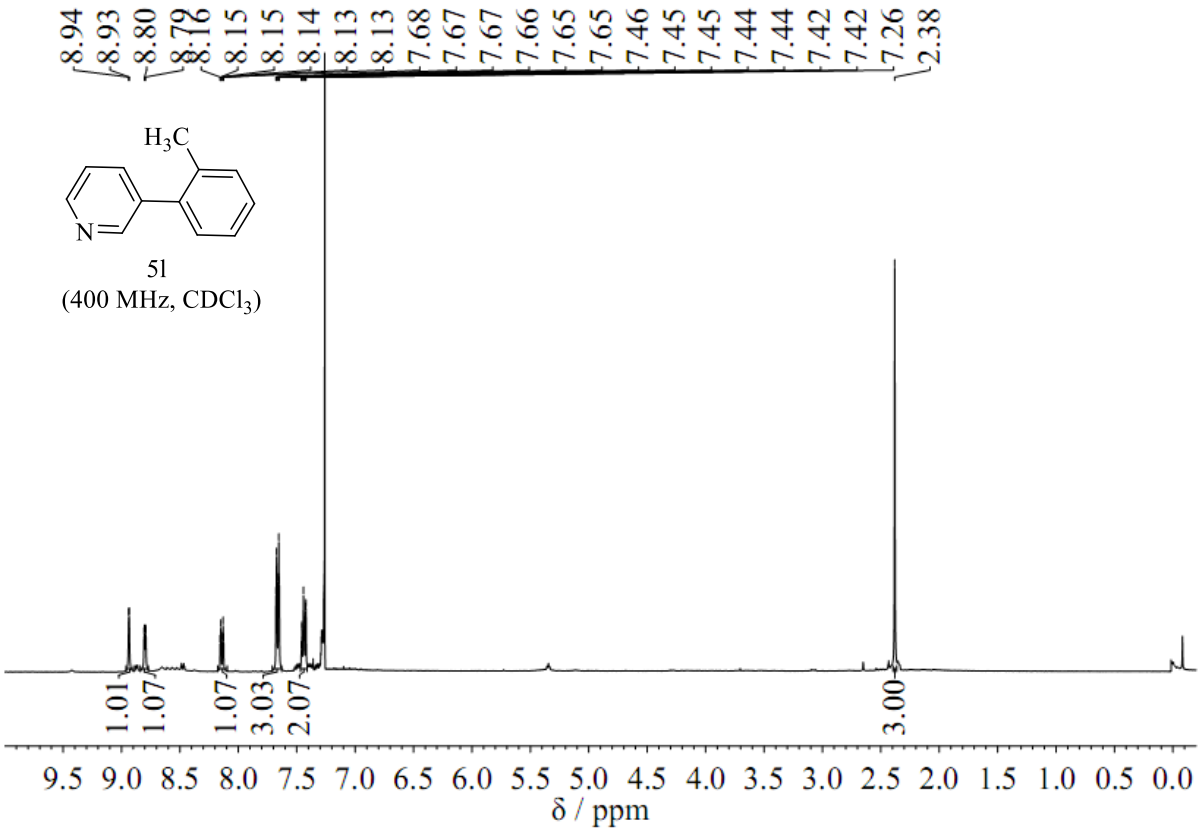
5j
(400 MHz, $CDCl_3$)

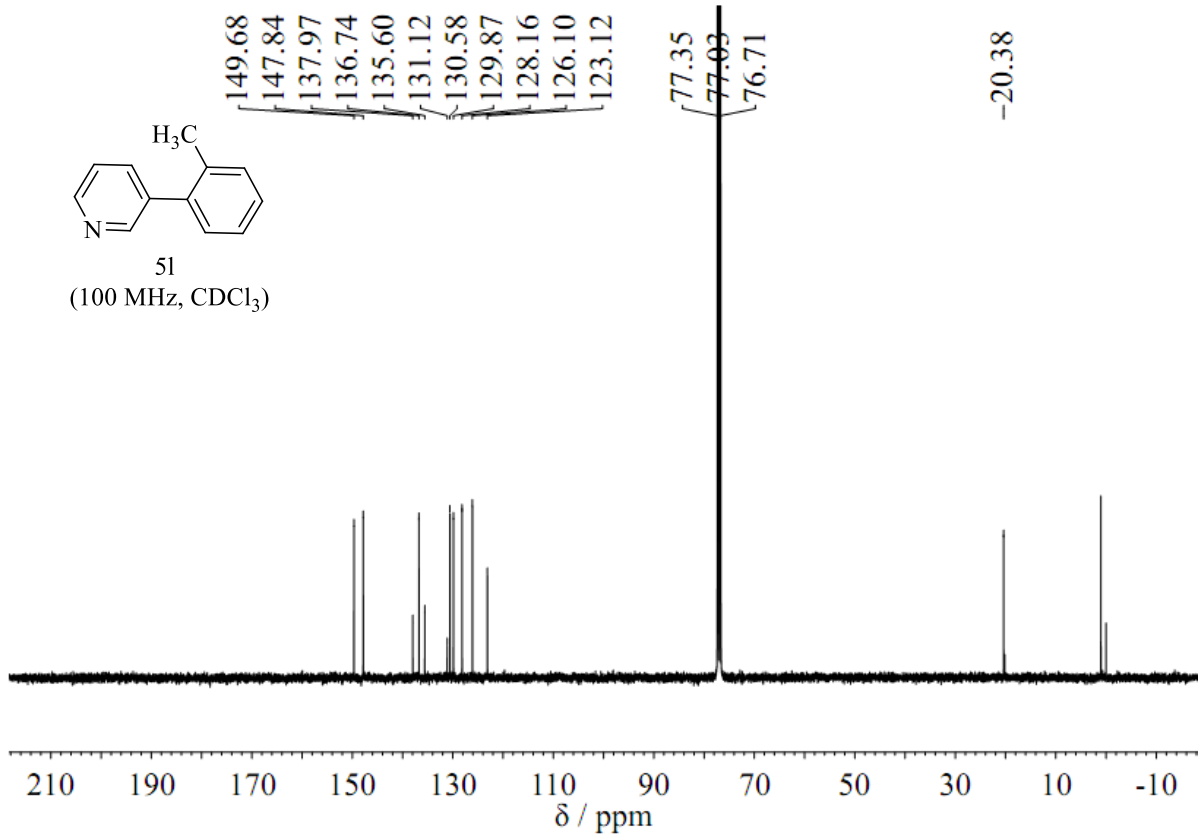


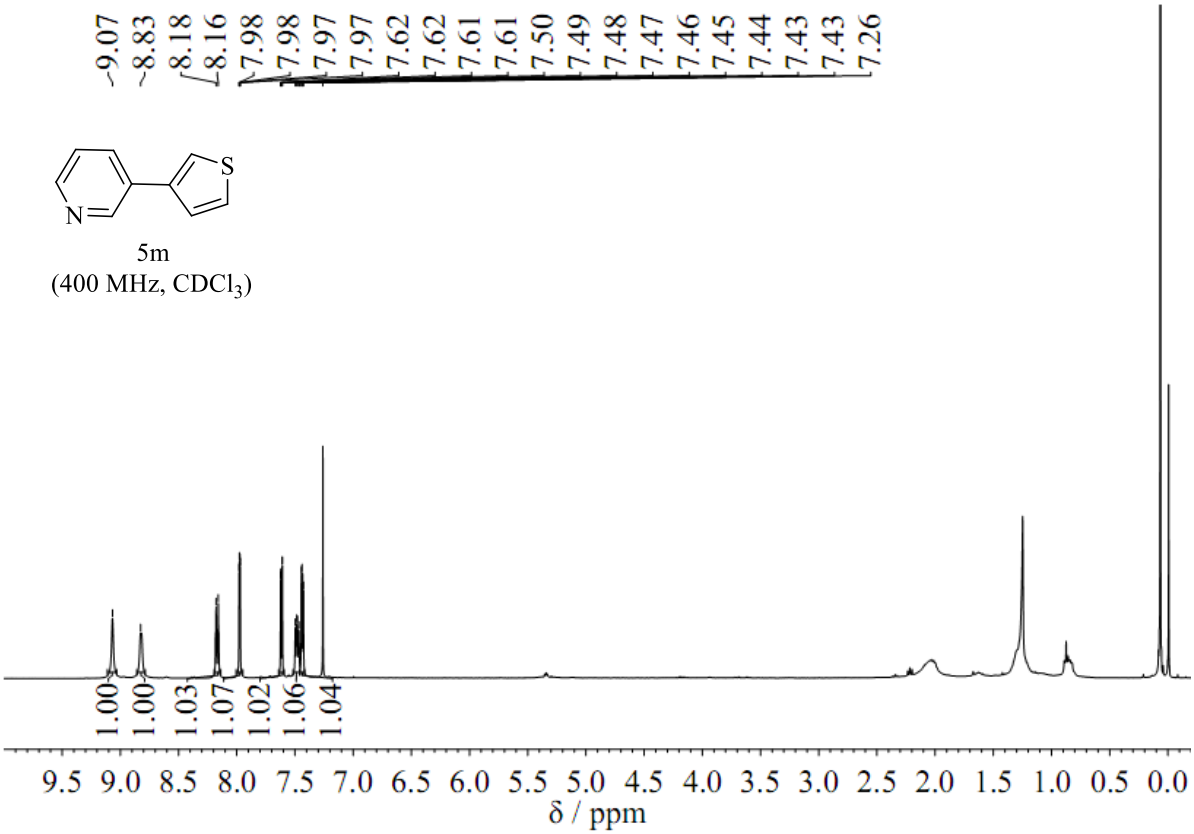
5j
(100 MHz, $CDCl_3$)


8.78
8.71
7.95
7.93
7.91
7.85
7.84
7.82
7.80
7.58
7.56
7.56
7.54
7.53
7.53
7.51
7.51
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.43
7.42
7.42
N
5k
(400 MHz, CDCl3)
2.00
1.86
1.92
1.64
0.75
1.32
1.10
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
δ / ppm

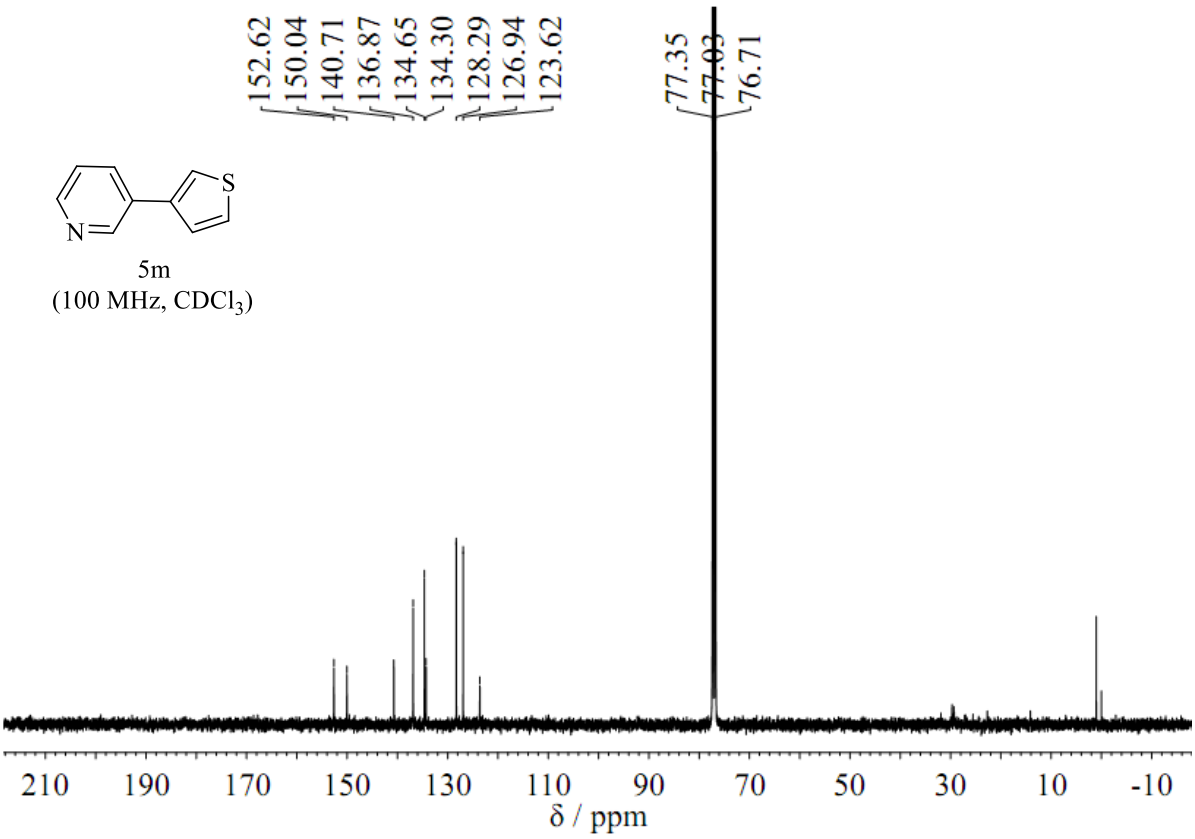

150.57
148.40
137.55
136.26
133.81
131.47
128.60
128.51
127.44
126.60
126.14
125.42
125.28
124.33
123.25
77.35
77.03
76.71
N
5k
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.94
8.93
8.80
8.79
8.16
8.15
8.15
8.14
8.13
8.13
7.68
7.67
7.67
7.66
7.65
7.65
7.46
7.45
7.45
7.44
7.44
7.42
7.42
7.26
2.38
H3C
N
5l
(400 MHz, CDCl3)
1.01
1.07
1.07
3.03
2.07
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
δ / ppm

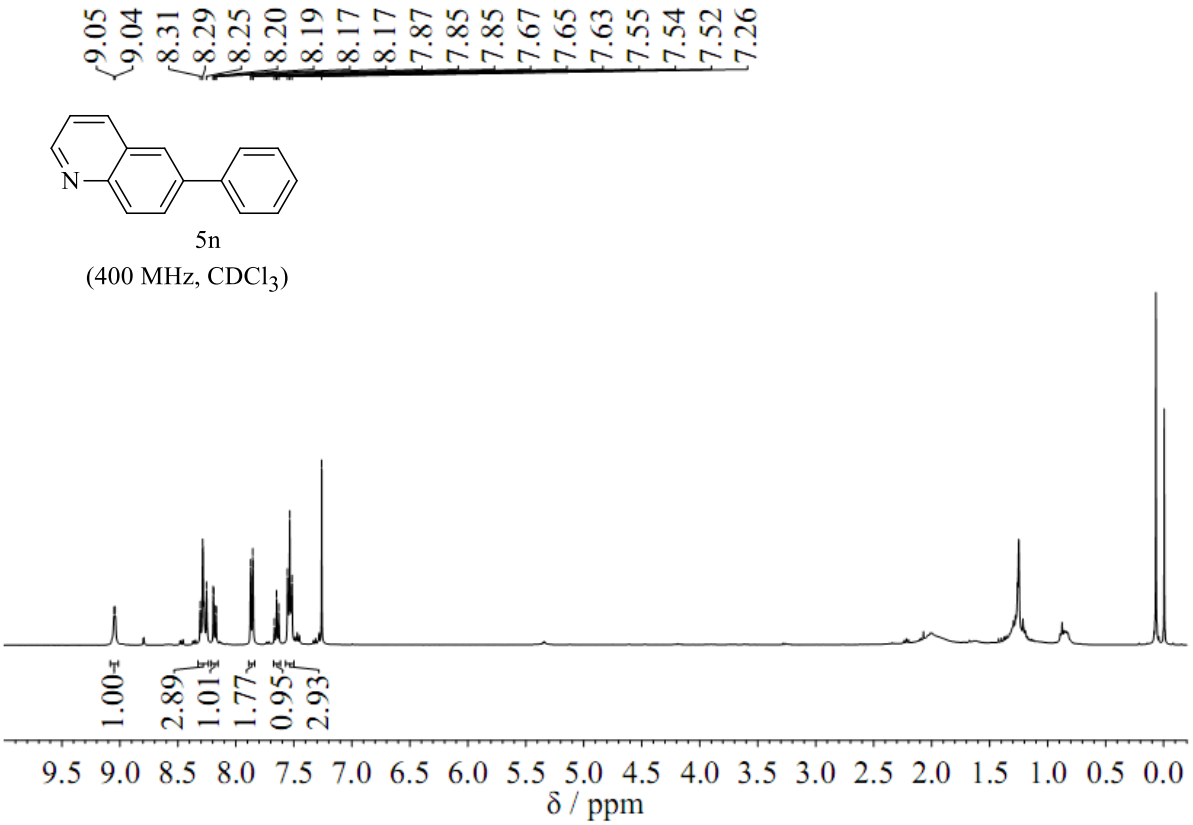

149.68
147.84
137.97
136.74
135.60
131.12
130.58
129.87
128.16
126.10
123.12
77.35
77.03
76.71
20.38
H3C
N
5l
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



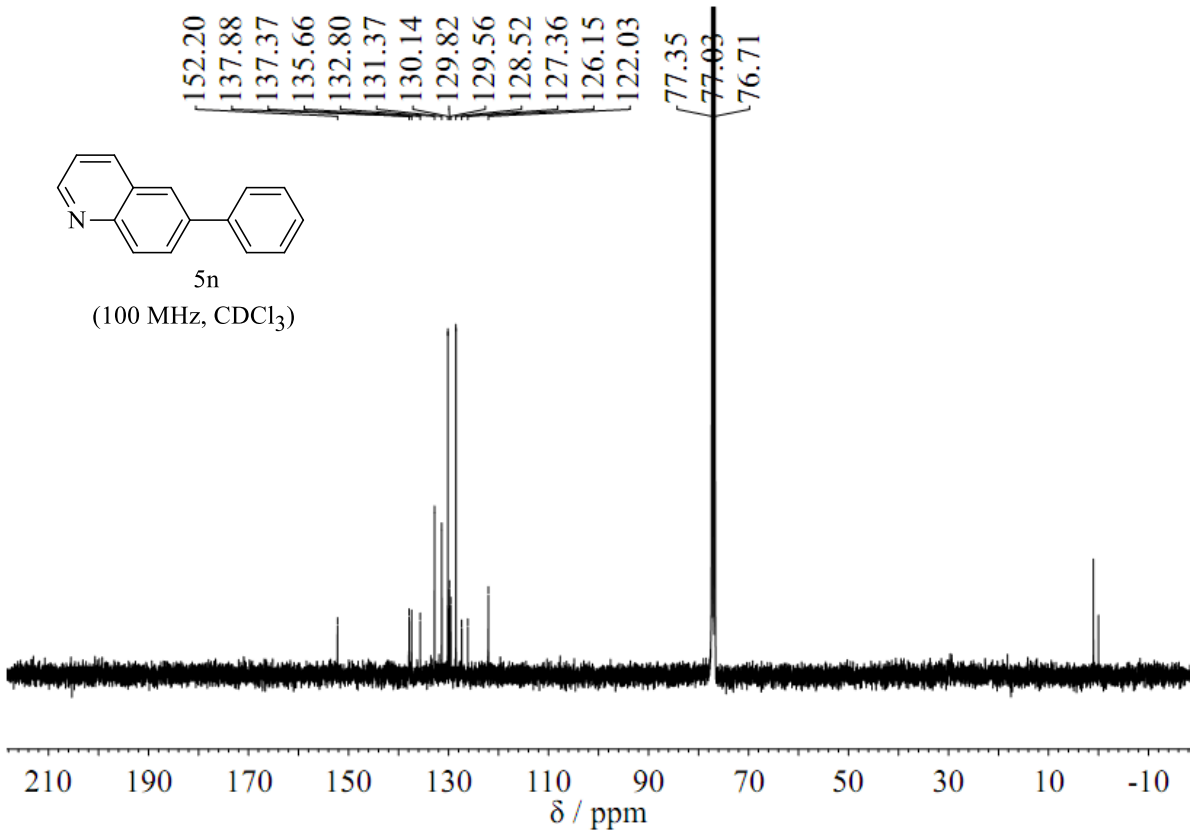
5m
(400 MHz, $CDCl_3$)



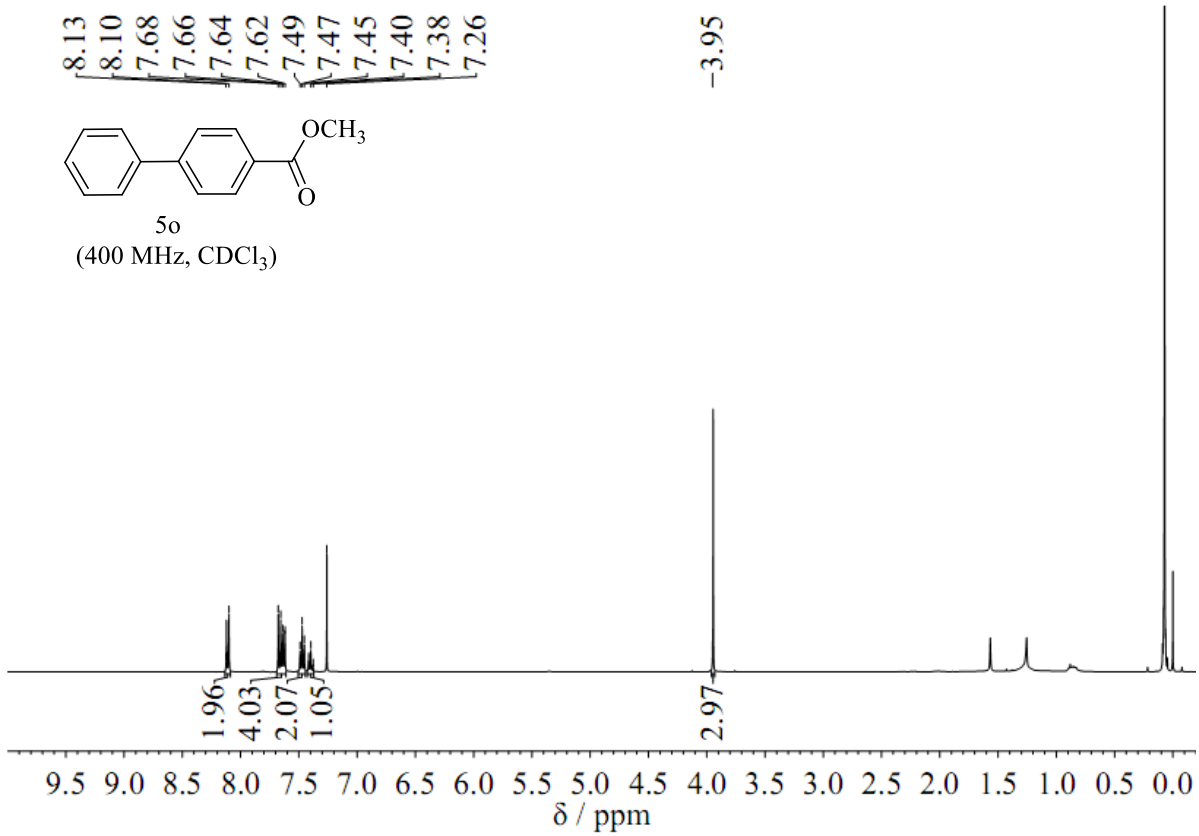
5m
(100 MHz, $CDCl_3$)



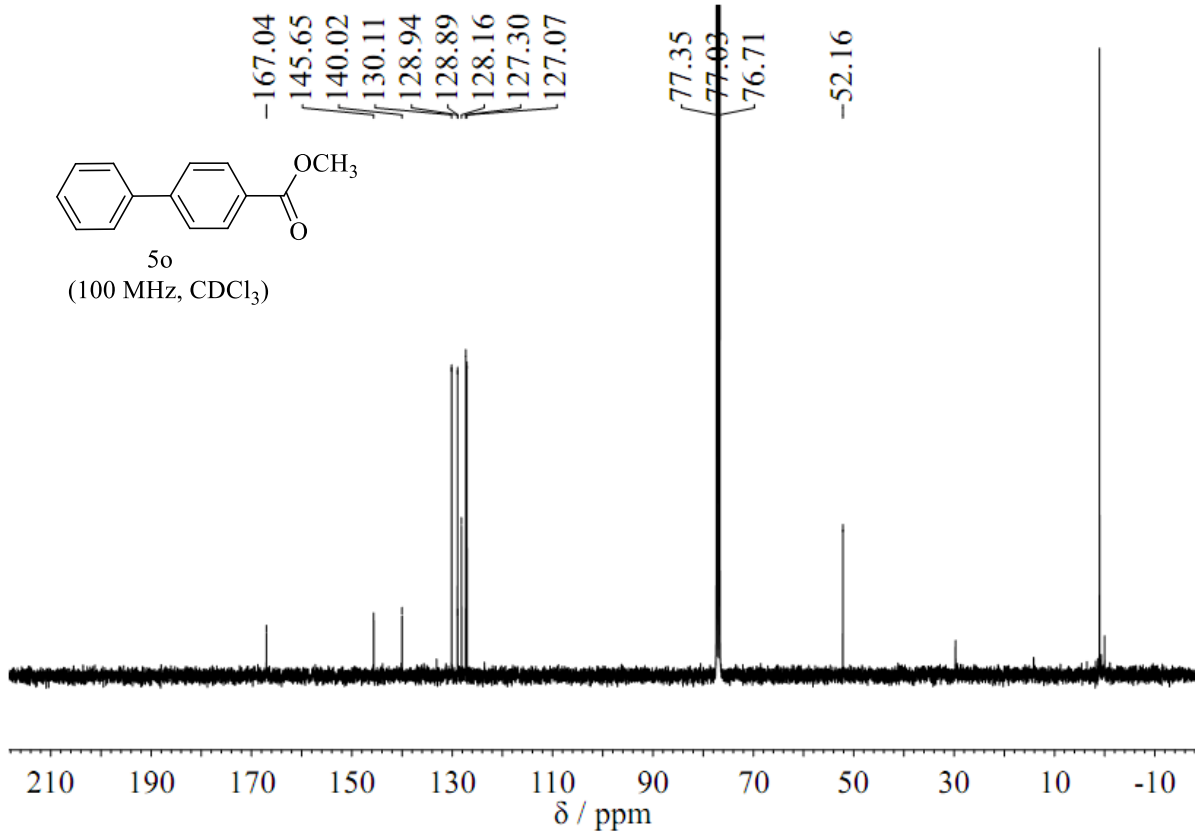
5n
(400 MHz, $CDCl_3$)



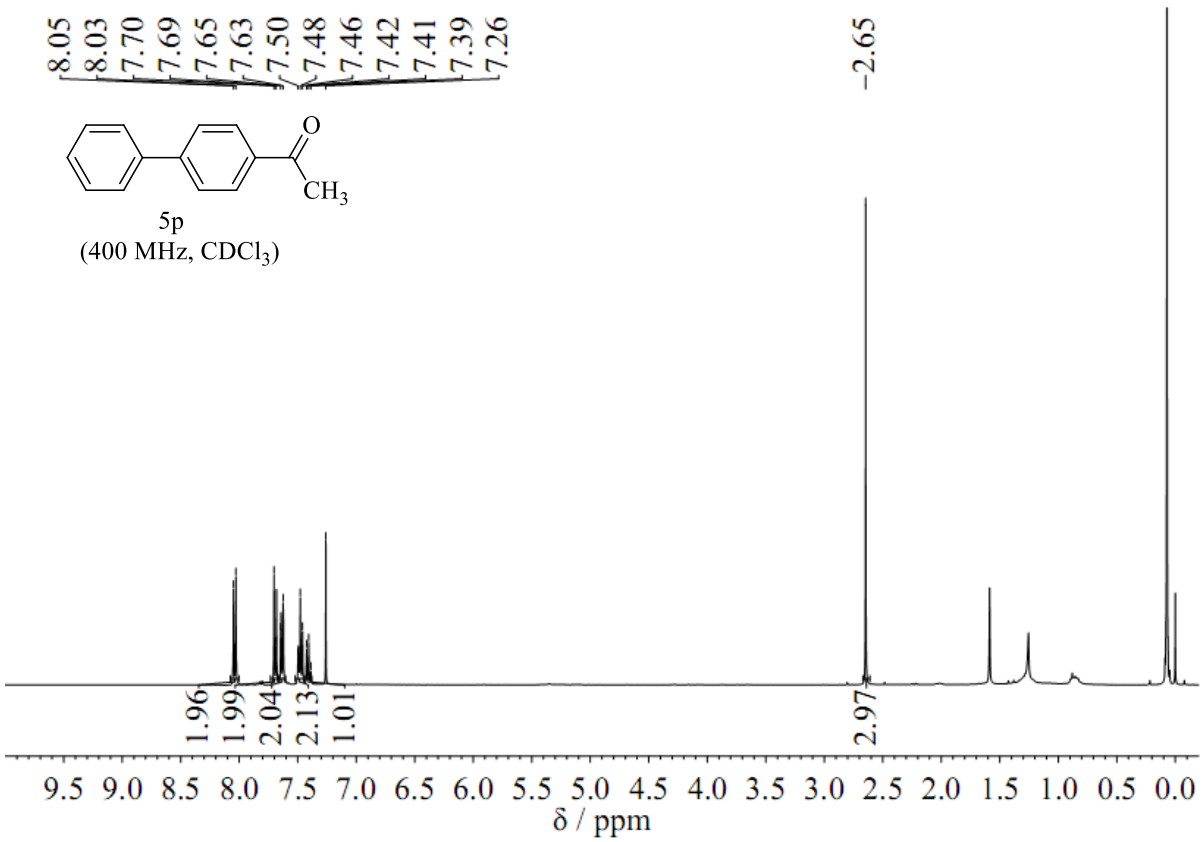
5n
(100 MHz, $CDCl_3$)



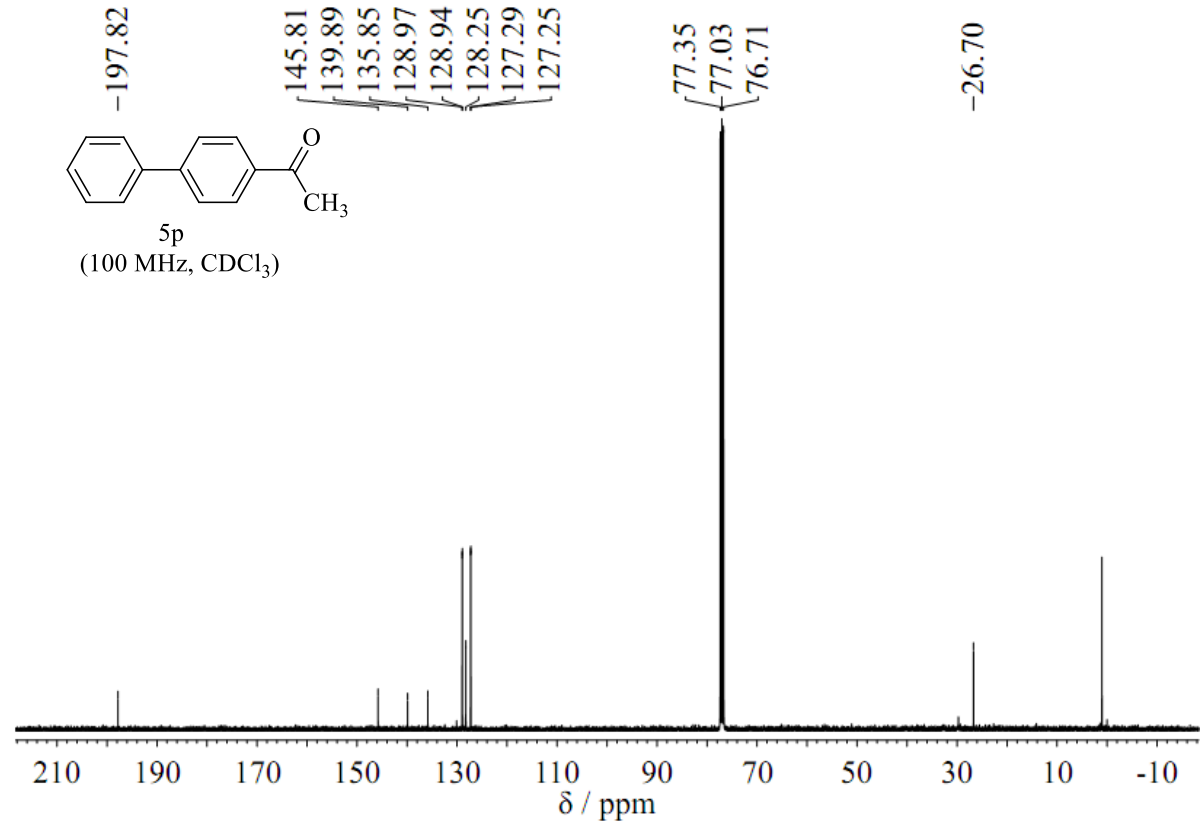
5o
(400 MHz, $CDCl_3$)



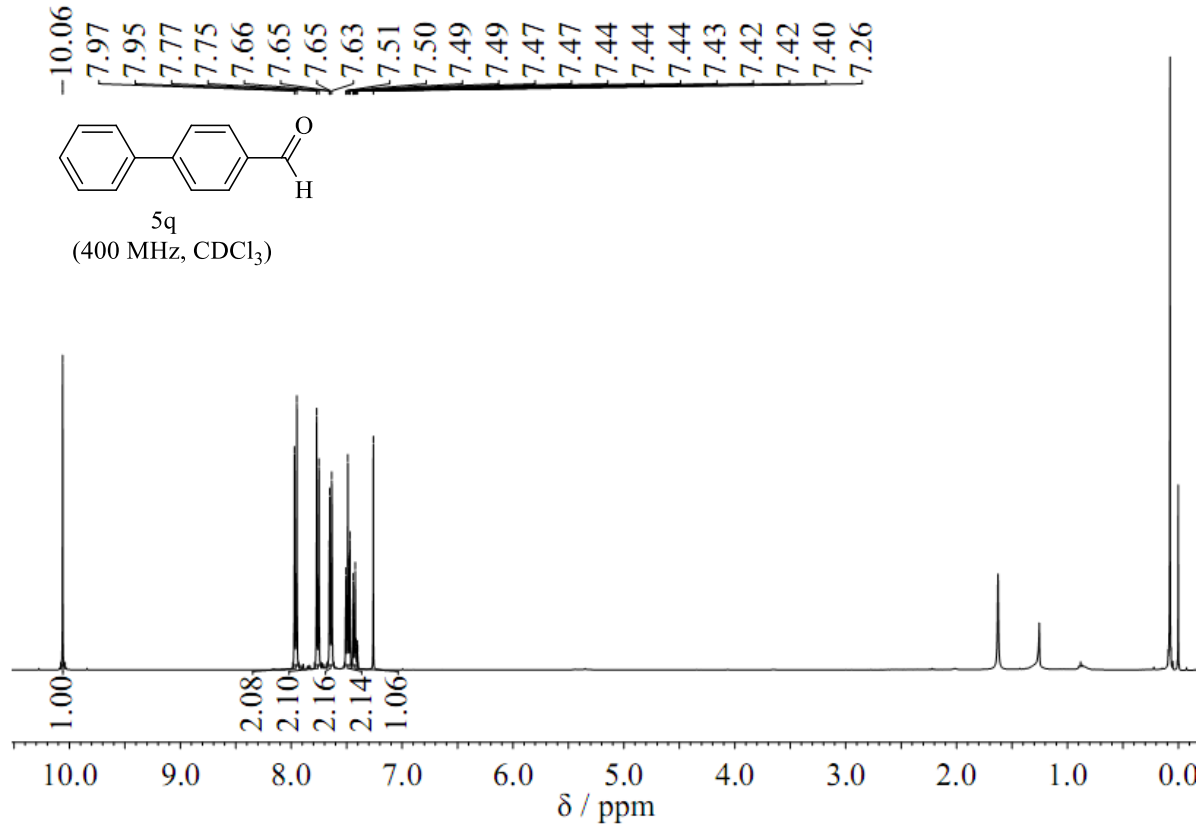
5o
(100 MHz, $CDCl_3$)



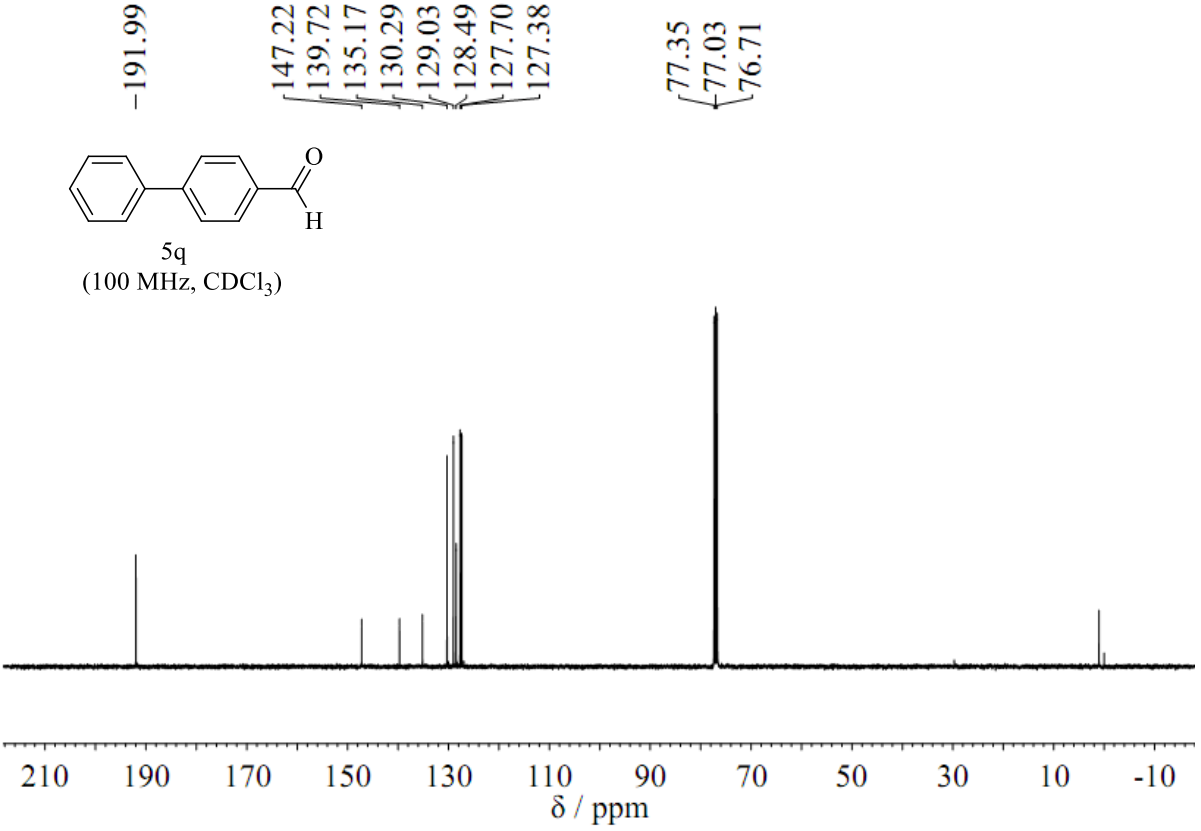
5p
(400 MHz, $CDCl_3$)



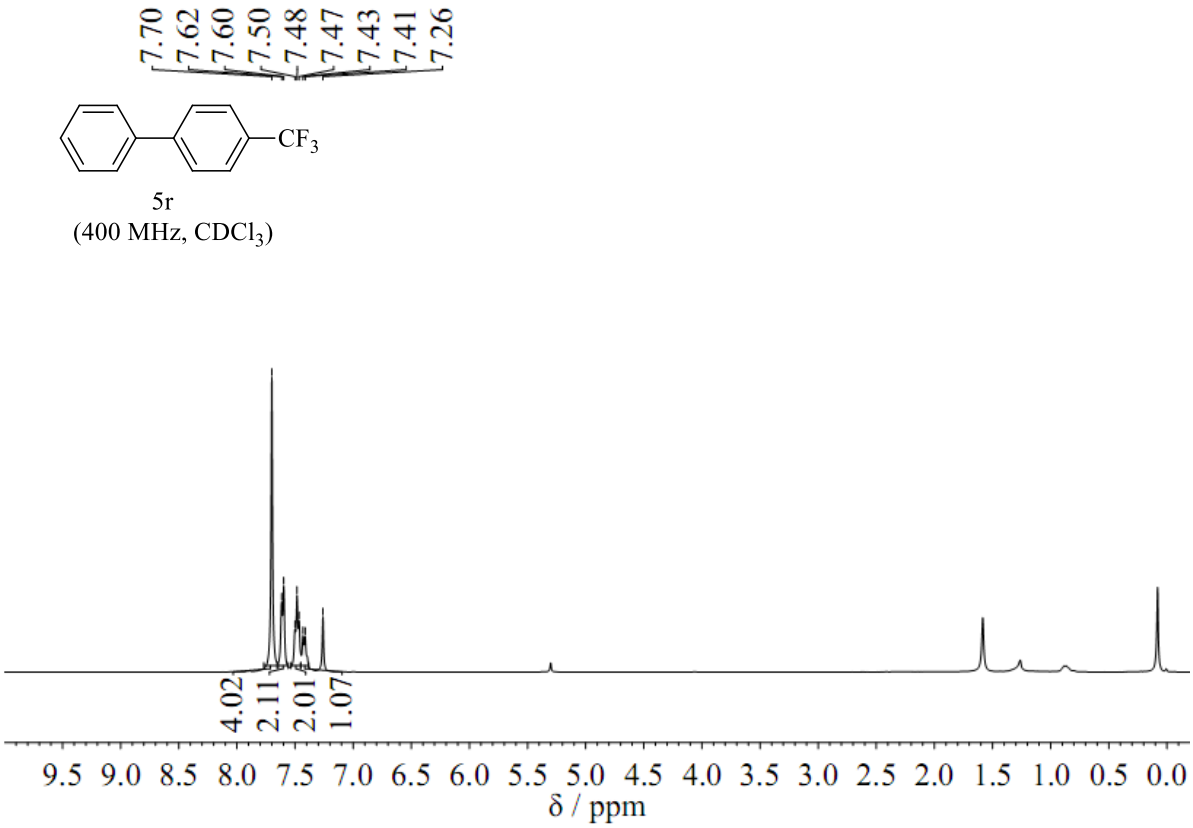
5p
(100 MHz, $CDCl_3$)



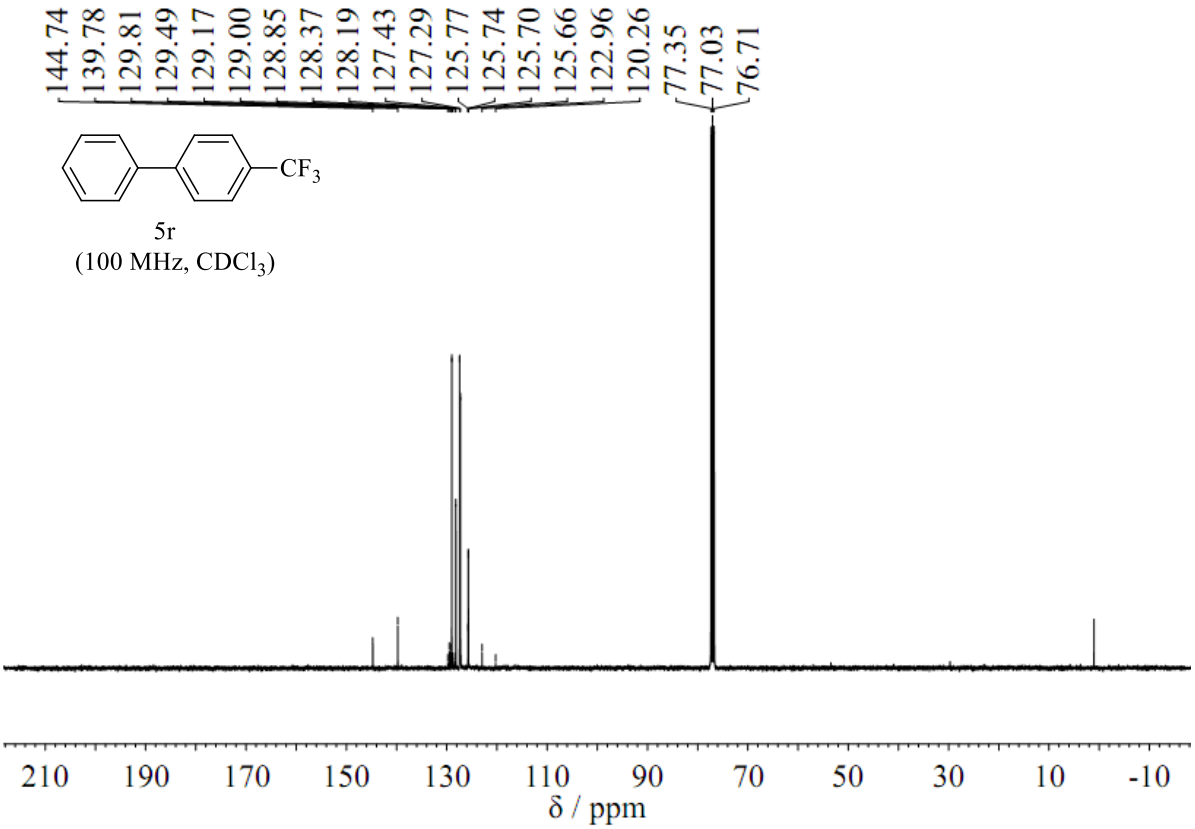
5q
(400 MHz, $CDCl_3$)



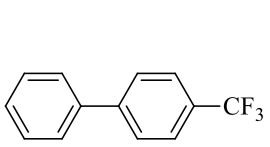
5q
(100 MHz, $CDCl_3$)



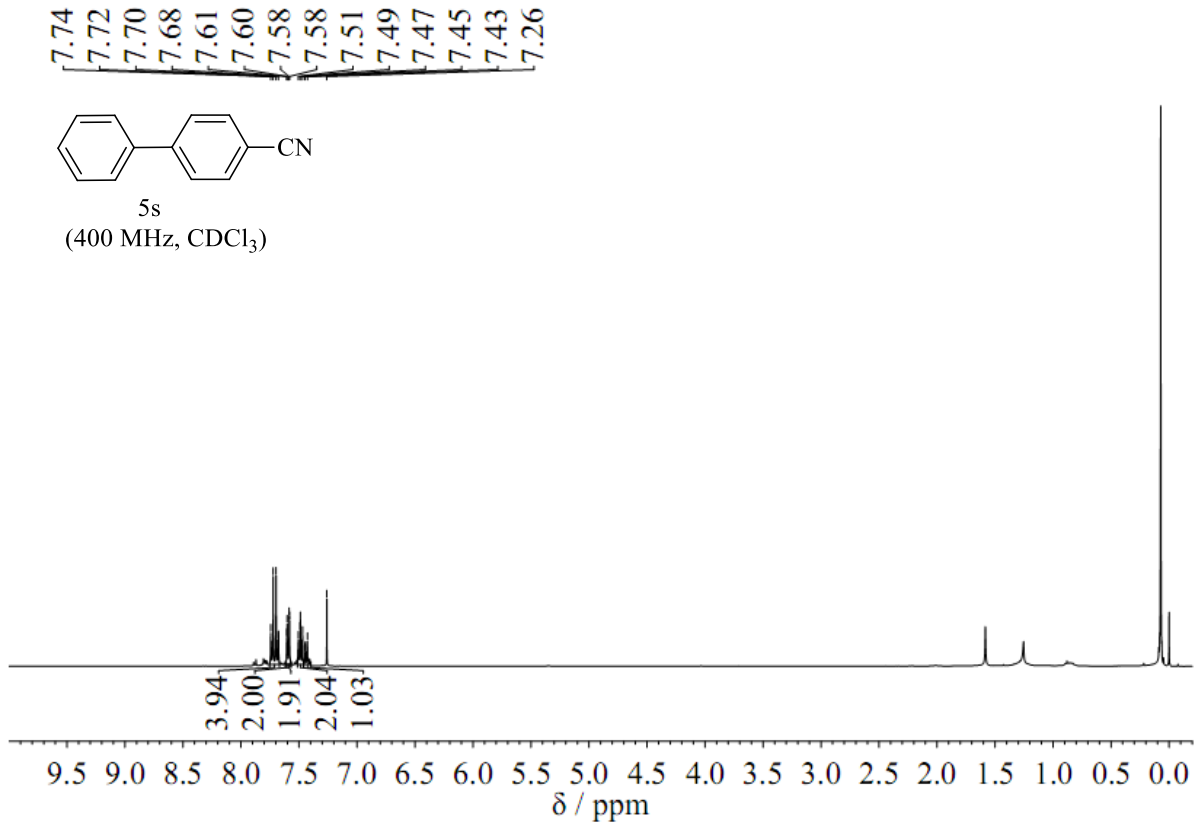
5r
(400 MHz, $CDCl_3$)

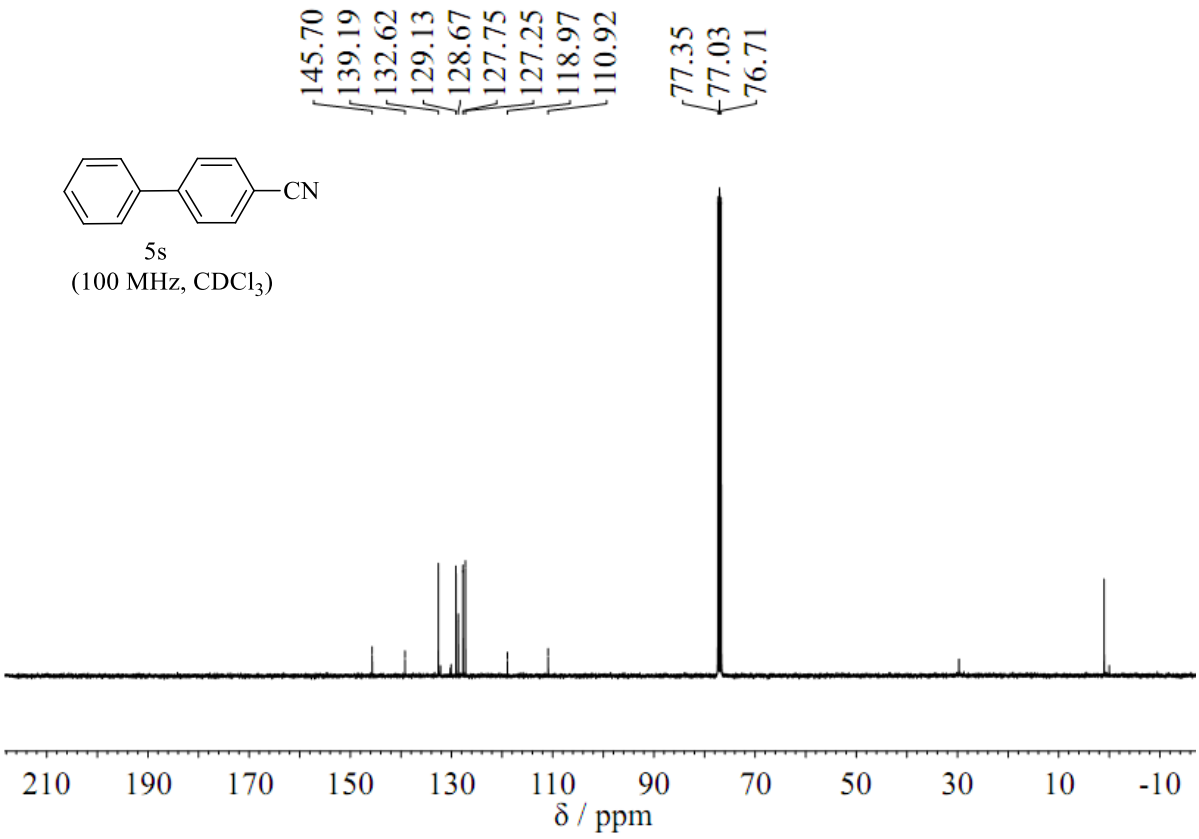


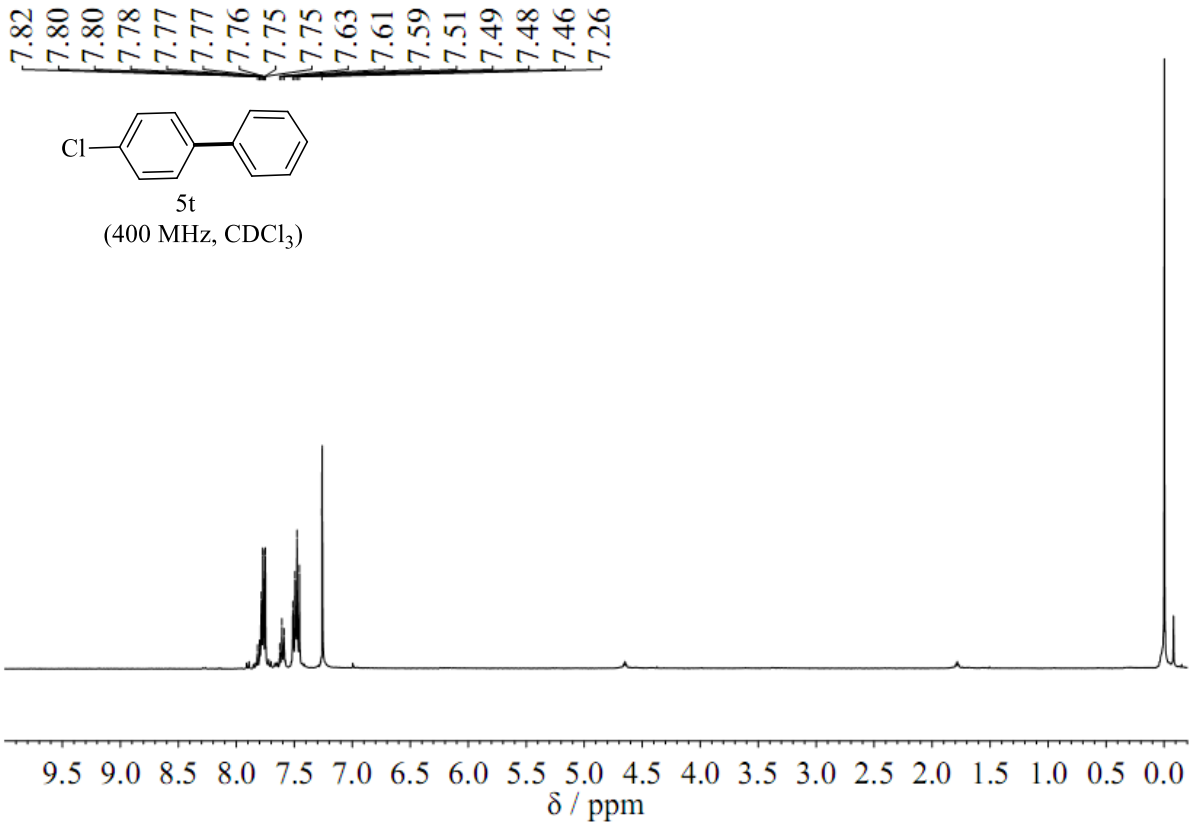
5r
(100 MHz, $CDCl_3$)



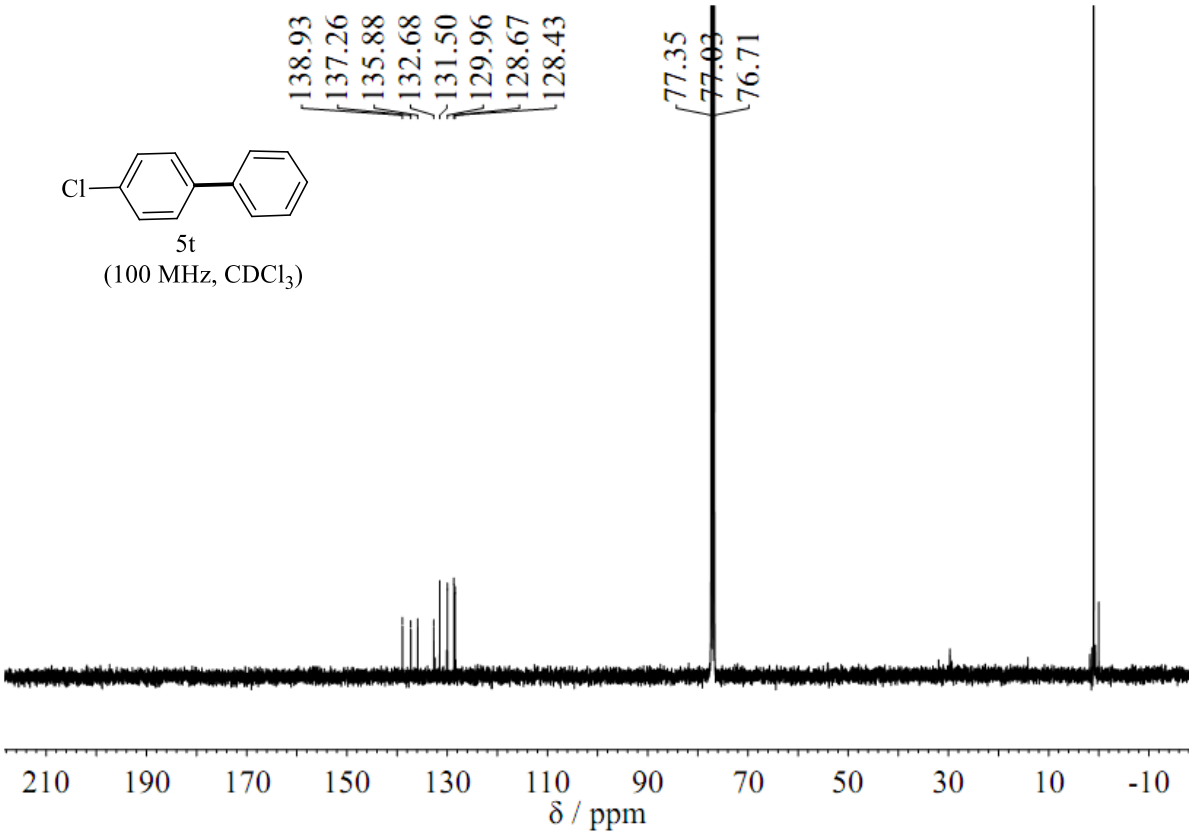
5r
(376 MHz, $CDCl_3$)


7.74
7.72
7.70
7.68
7.61
7.60
7.58
7.58
7.51
7.49
7.47
7.45
7.43
7.26
CN
5s
(400 MHz, CDCl3)
3.94
2.00
1.91
2.04
1.03
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
δ / ppm

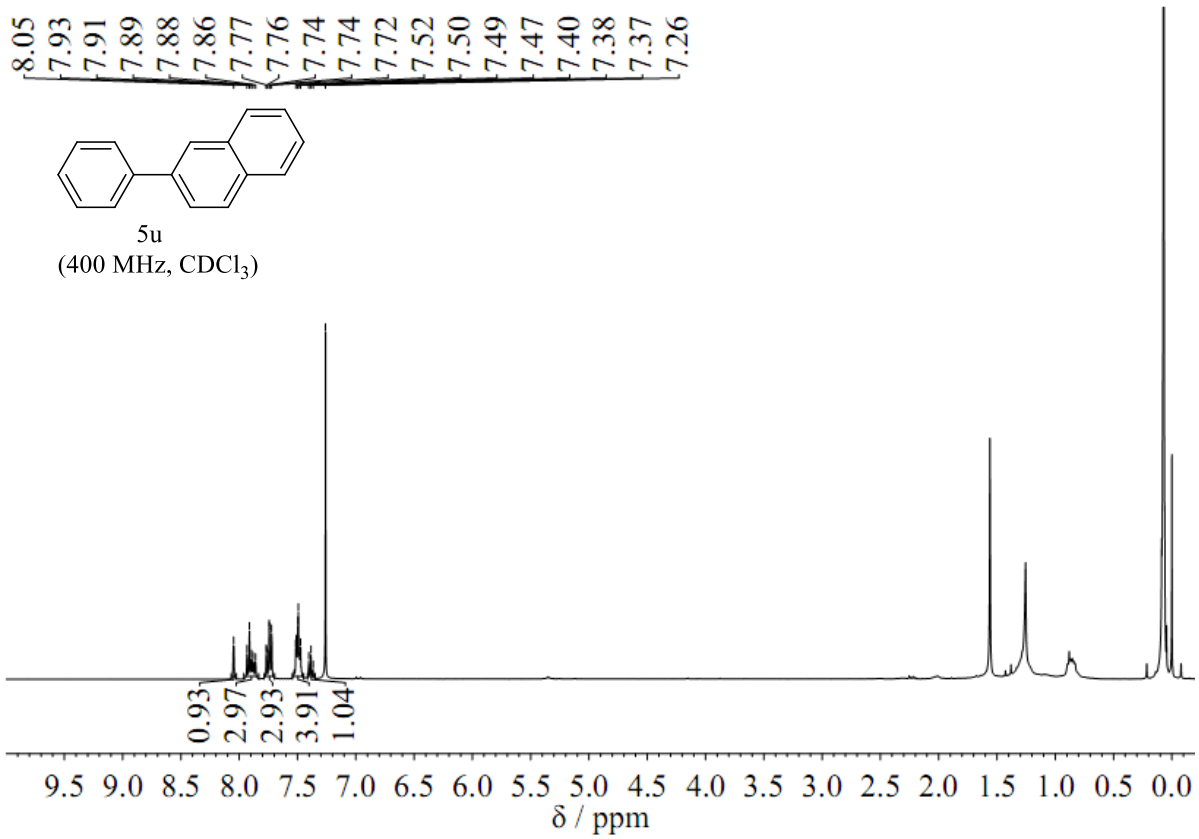

145.70
139.19
132.62
129.13
128.67
127.75
127.25
118.97
110.92
77.35
77.03
76.71
CN
5s
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



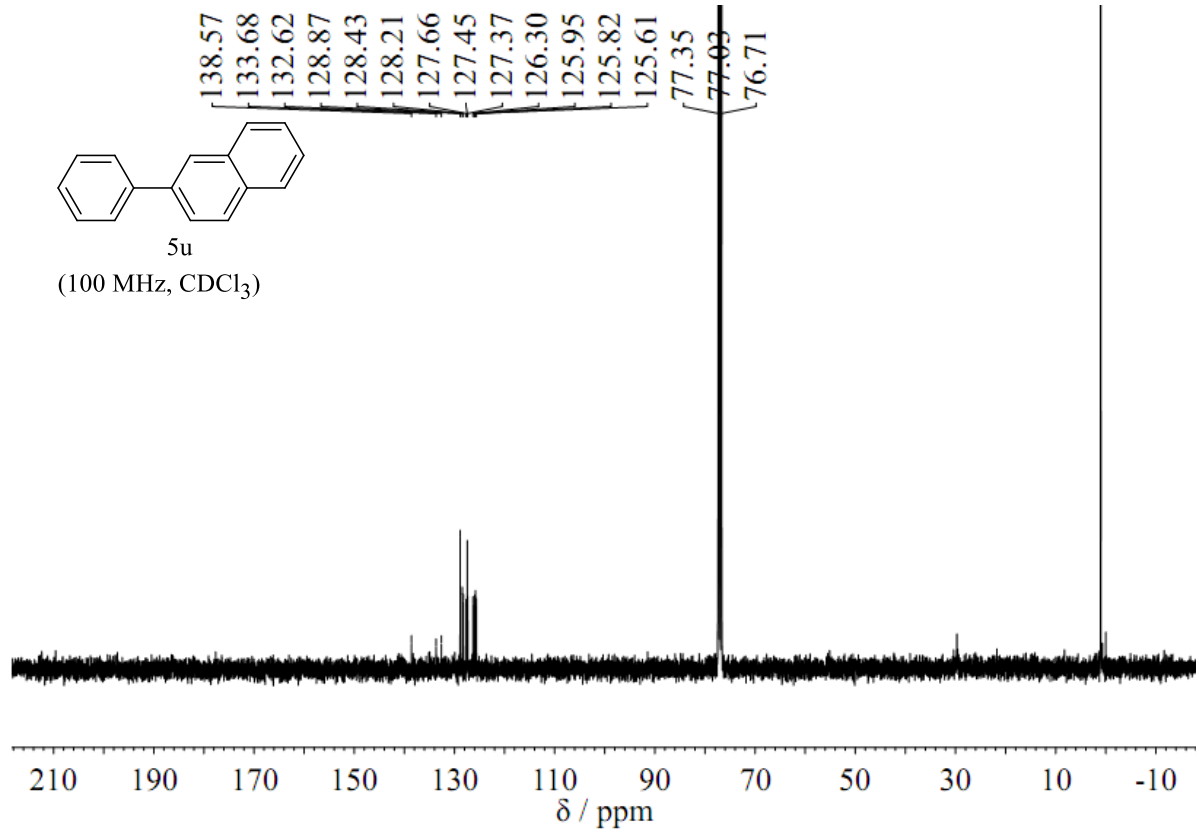
5t
(400 MHz, $CDCl_3$)



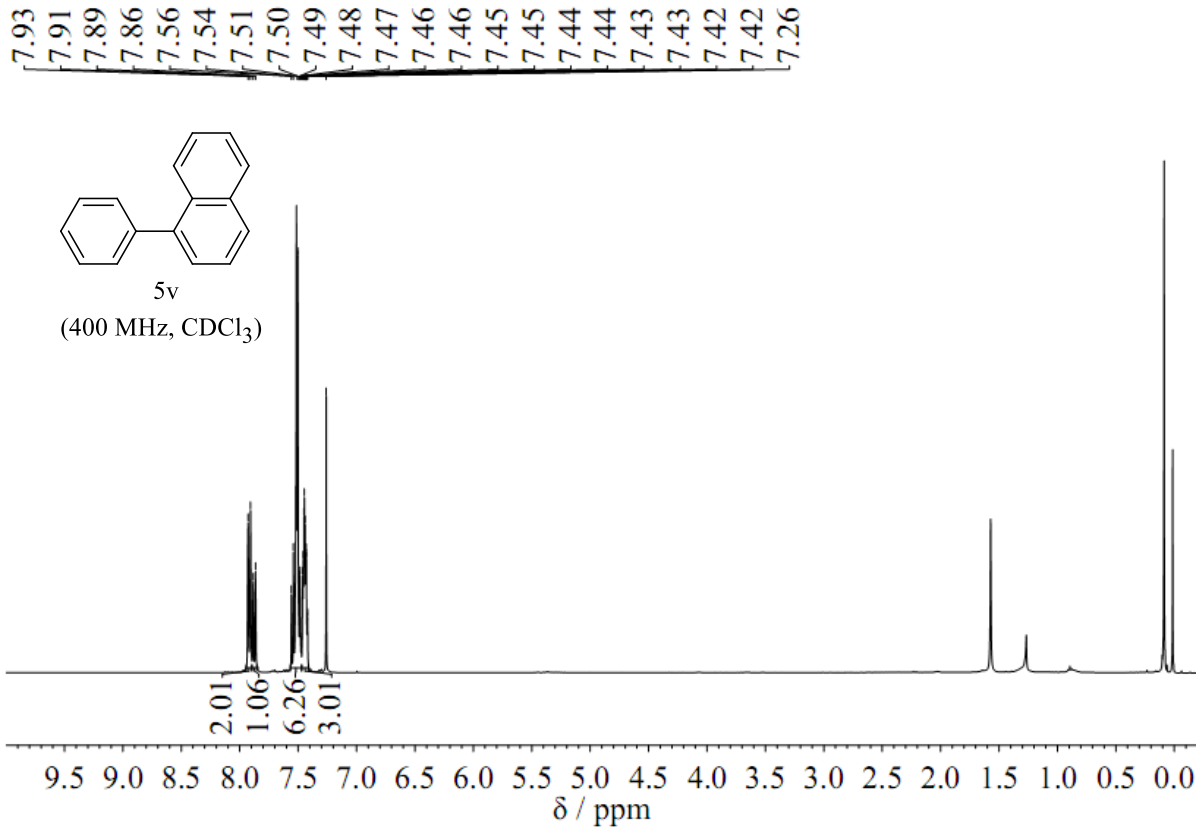
5t
(100 MHz, $CDCl_3$)

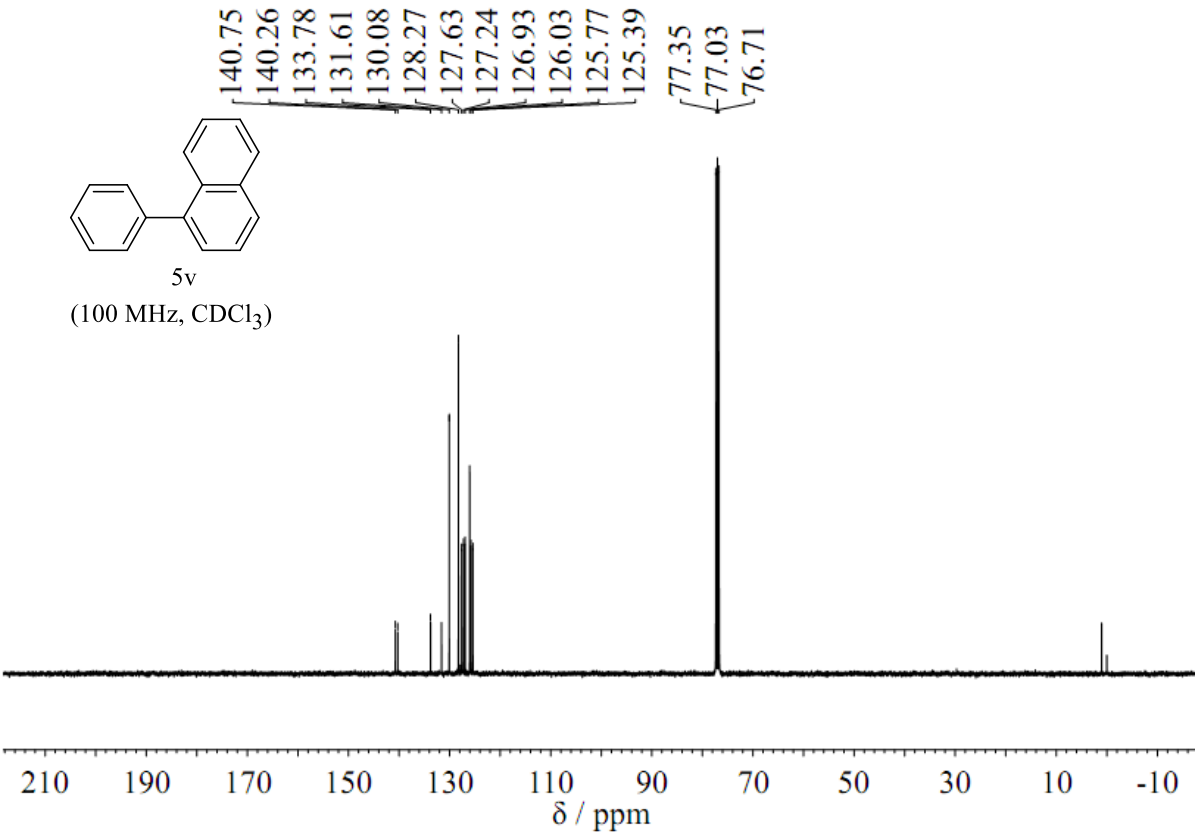


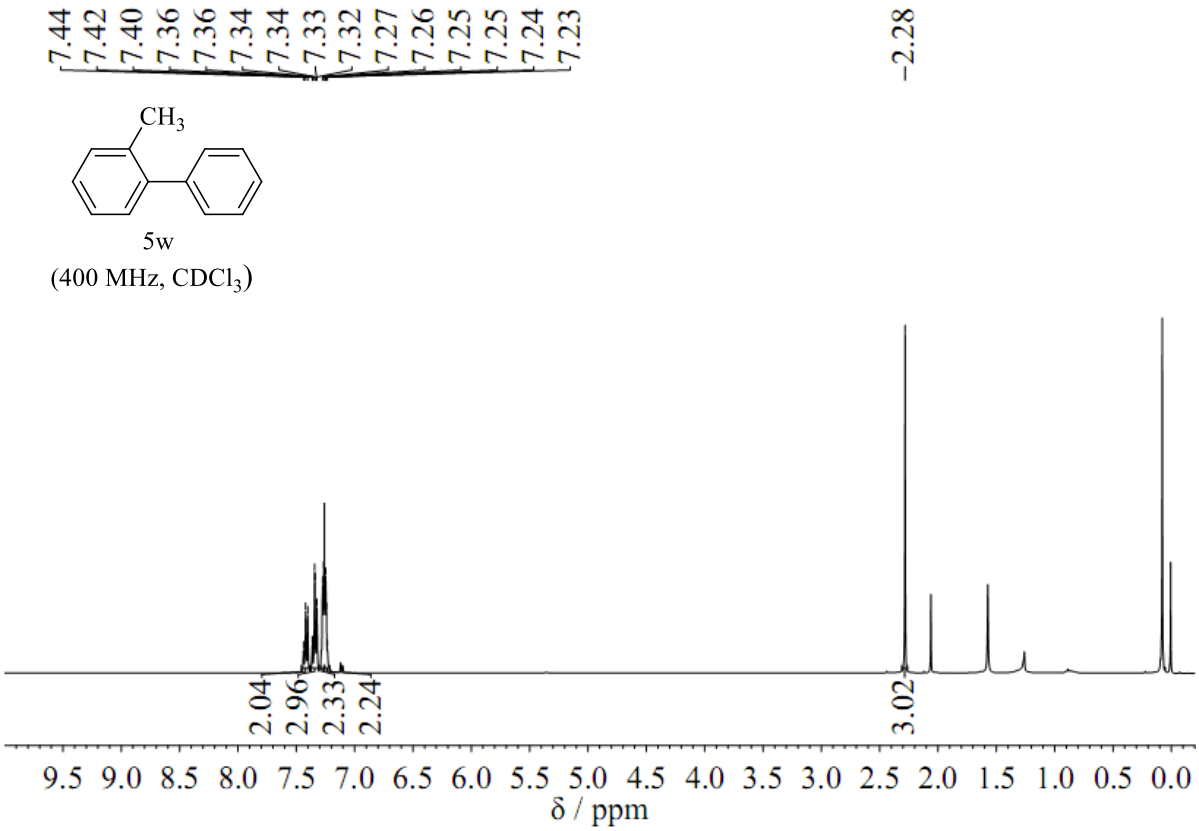
5u
(400 MHz, $CDCl_3$)

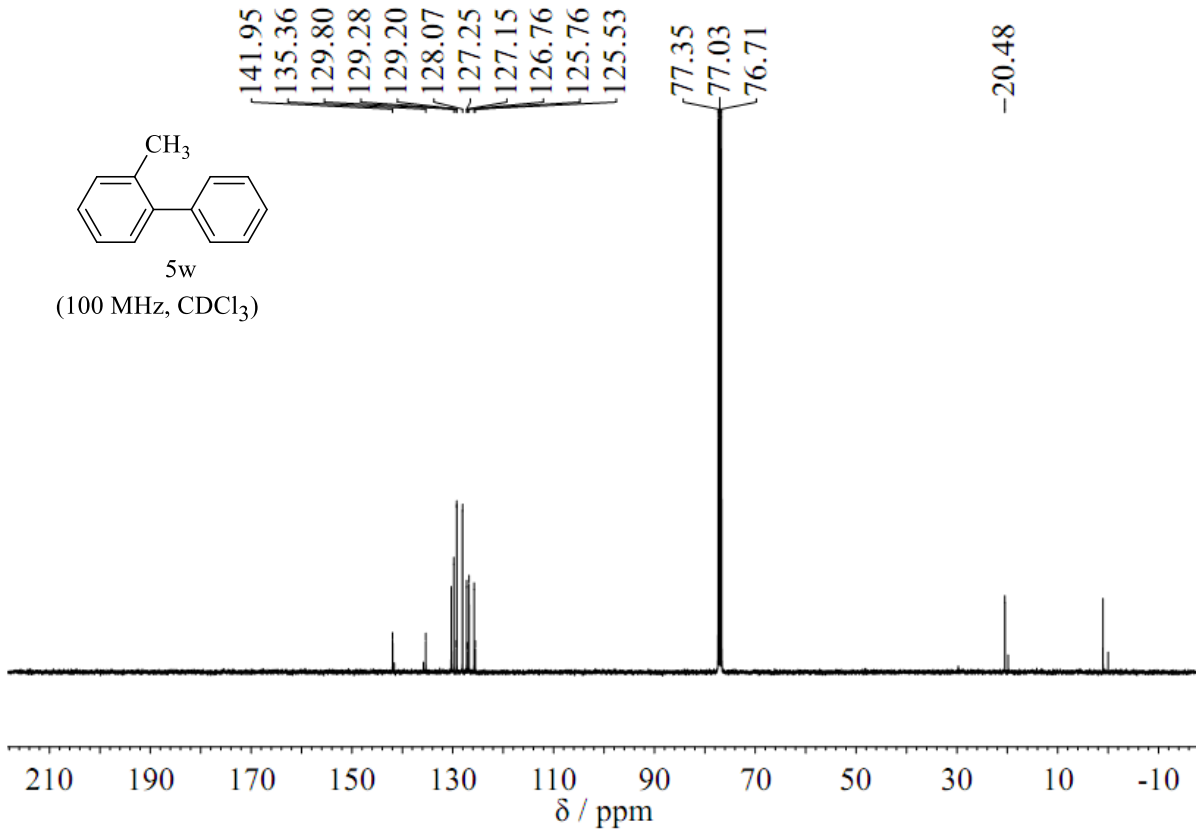


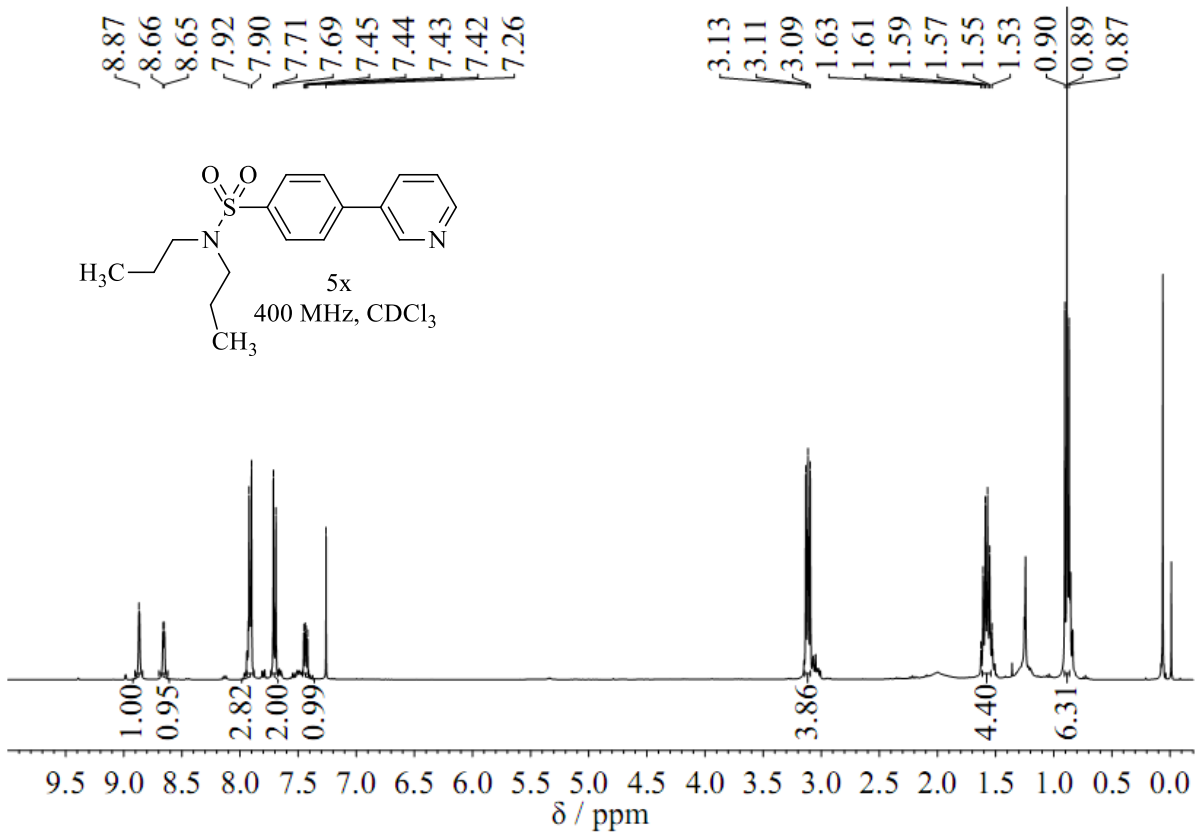
5u
(100 MHz, $CDCl_3$)

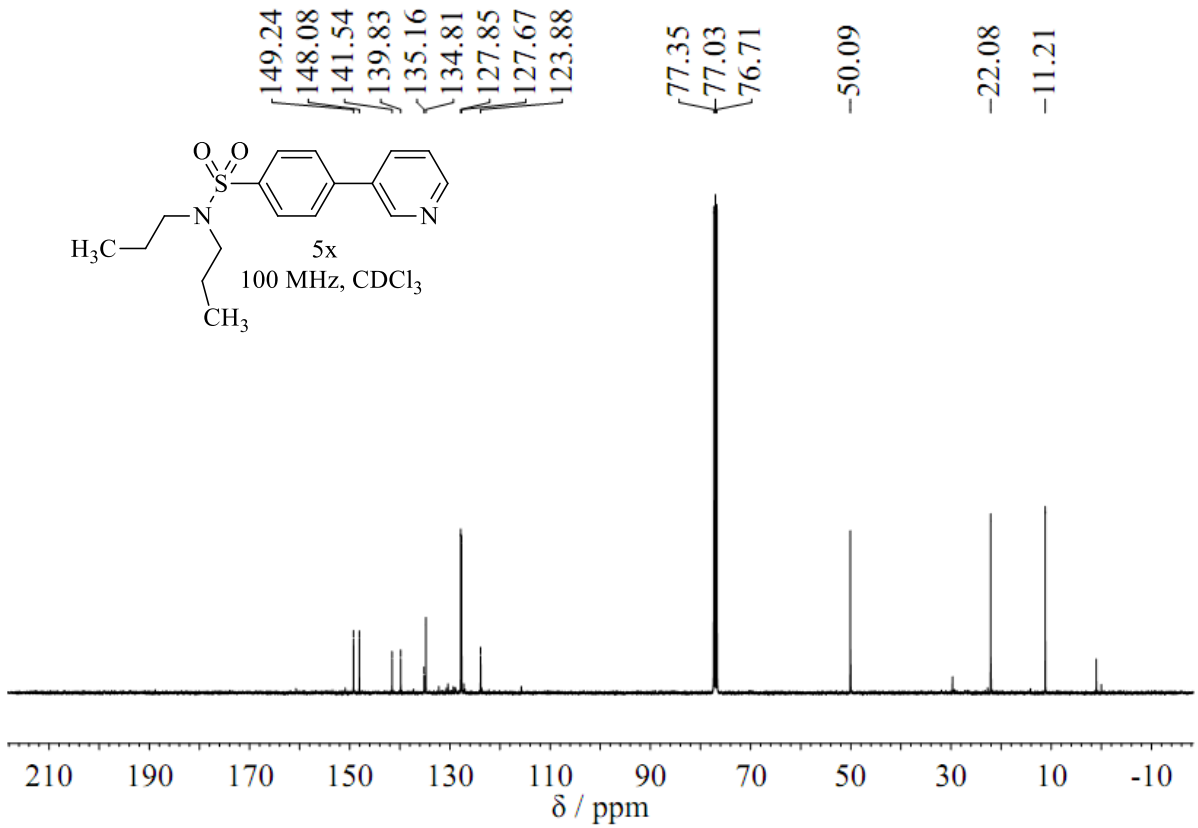

7.93
7.91
7.89
7.86
7.56
7.54
7.51
7.50
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.26
5v
(400 MHz, CDCl3)
2.01
1.06
6.26
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

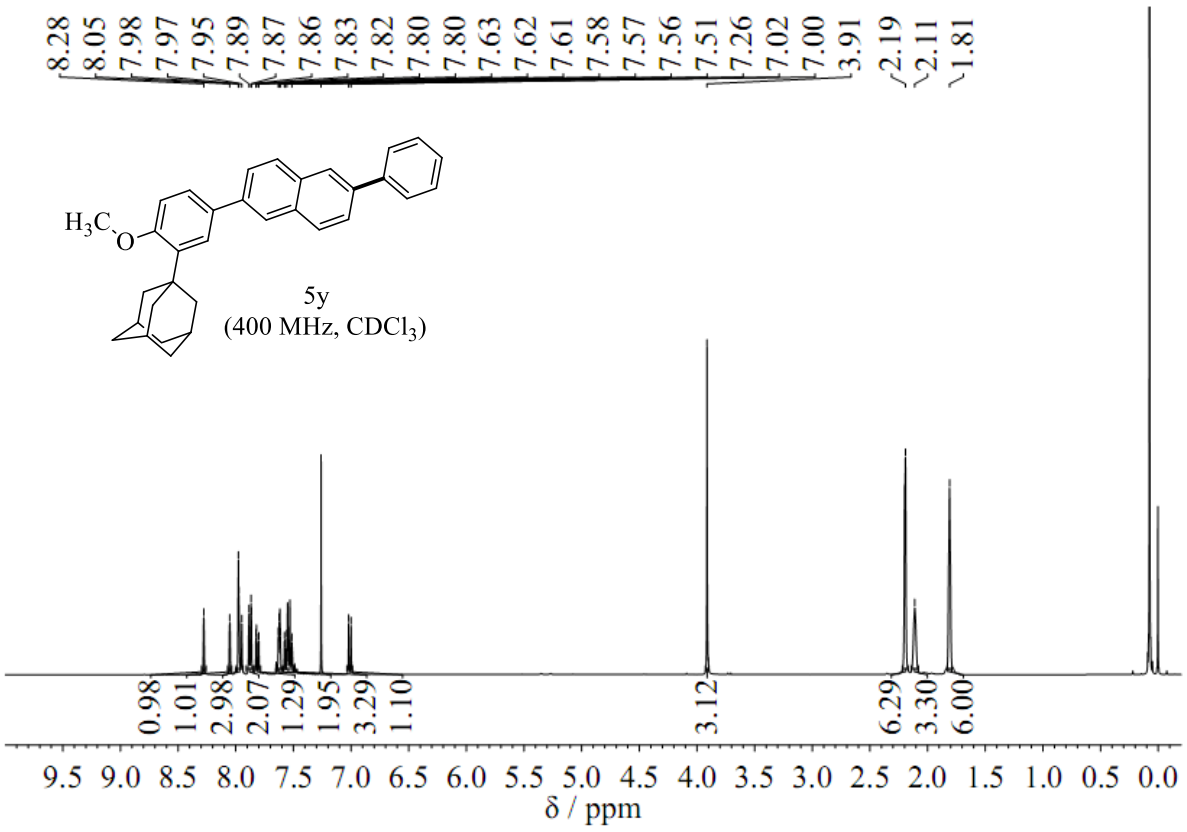

140.75
140.26
133.78
131.61
130.08
128.27
127.63
127.24
126.93
126.03
125.77
125.39
77.35
77.03
76.71
5v
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm

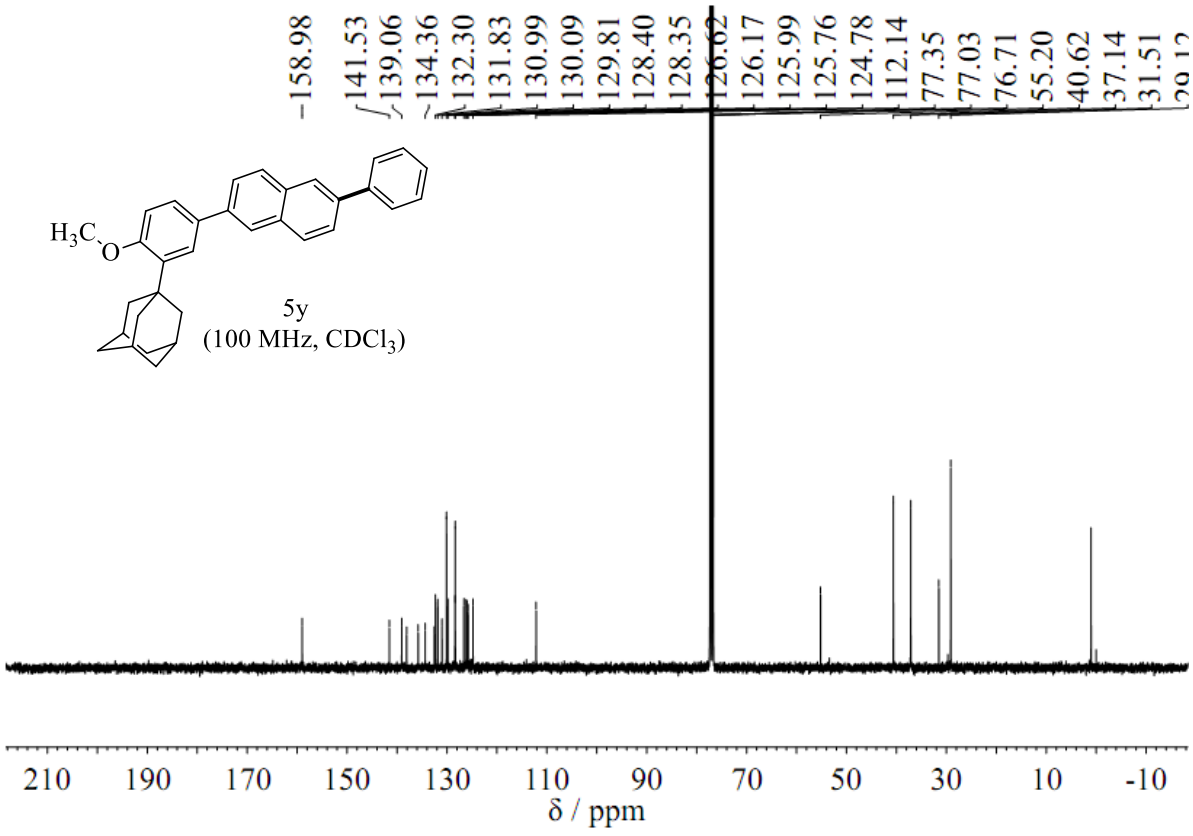

7.44
7.42
7.40
7.36
7.36
7.34
7.34
7.33
7.32
7.27
7.26
7.25
7.25
7.24
7.23
2.28
CH3
5w
(400 MHz, CDCl3)
2.04
2.96
2.33
2.24
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

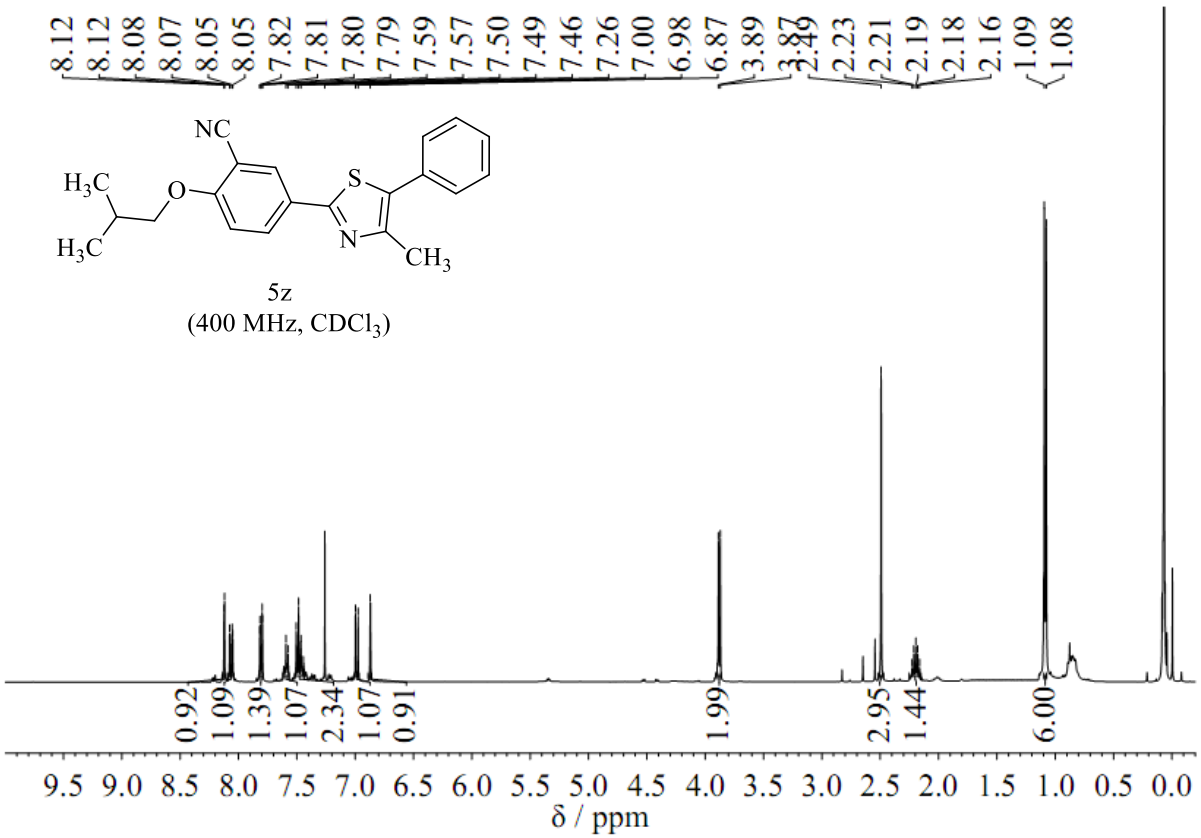

141.95
135.36
129.80
129.28
129.20
128.07
127.25
127.15
126.76
125.76
125.53
77.35
77.03
76.71
20.48
CH3
5w
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.87
8.66
8.65
7.92
7.90
7.71
7.69
7.45
7.44
7.43
7.42
7.26
3.13
3.11
3.09
1.63
1.61
1.59
1.57
1.55
1.53
0.90
0.89
0.87
5x
400 MHz, CDCl3
1.00
0.95
2.82
2.00
0.99
3.86
4.40
6.31
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
δ / ppm

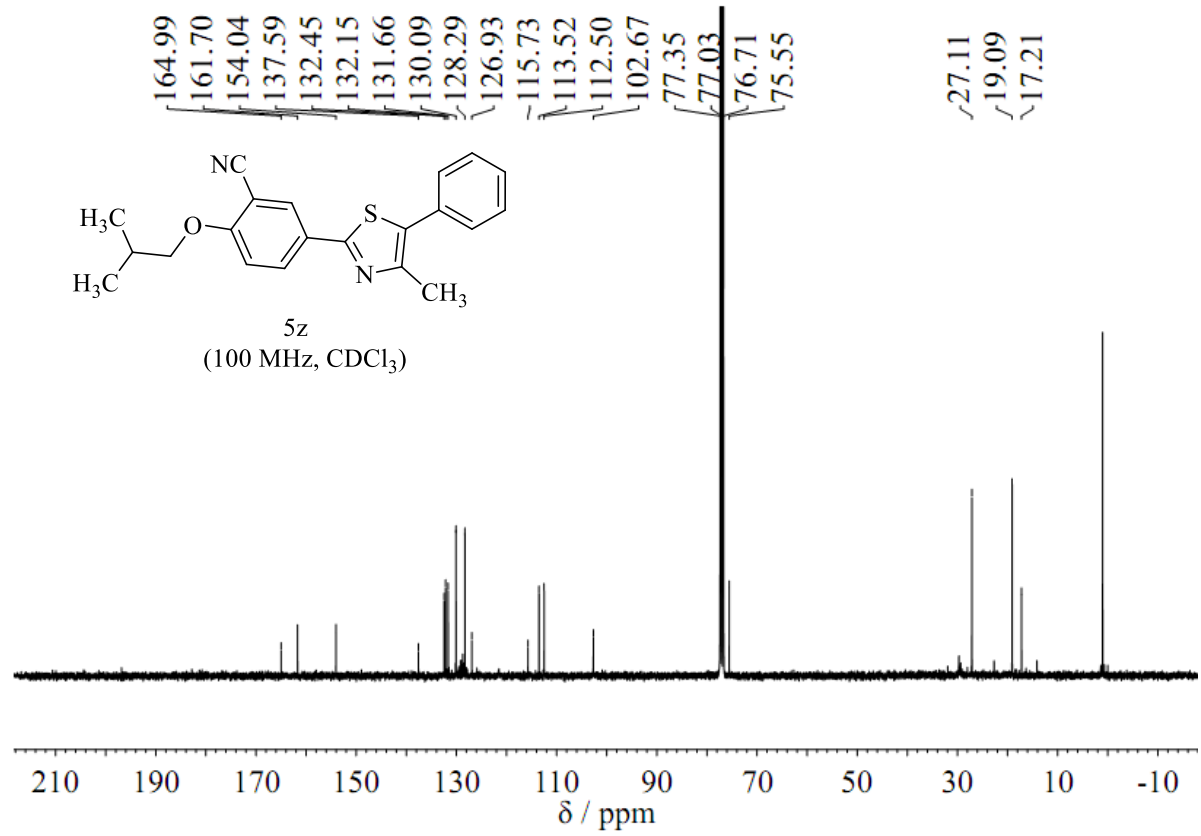

149.24
148.08
141.54
139.83
135.16
134.81
127.85
127.67
123.88
77.35
77.03
76.71
50.09
22.08
11.21
5x
100 MHz, CDCl3
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm


8.28
8.05
7.98
7.97
7.95
7.89
7.87
7.86
7.83
7.82
7.80
7.80
7.63
7.62
7.61
7.58
7.57
7.56
7.51
7.26
7.02
7.00
3.91
2.19
2.11
1.81
H3C
O
5y
(400 MHz, CDCl3)
0.98
1.01
2.98
2.07
1.29
1.95
3.29
1.10
3.12
6.29
3.30
6.00
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
δ / ppm

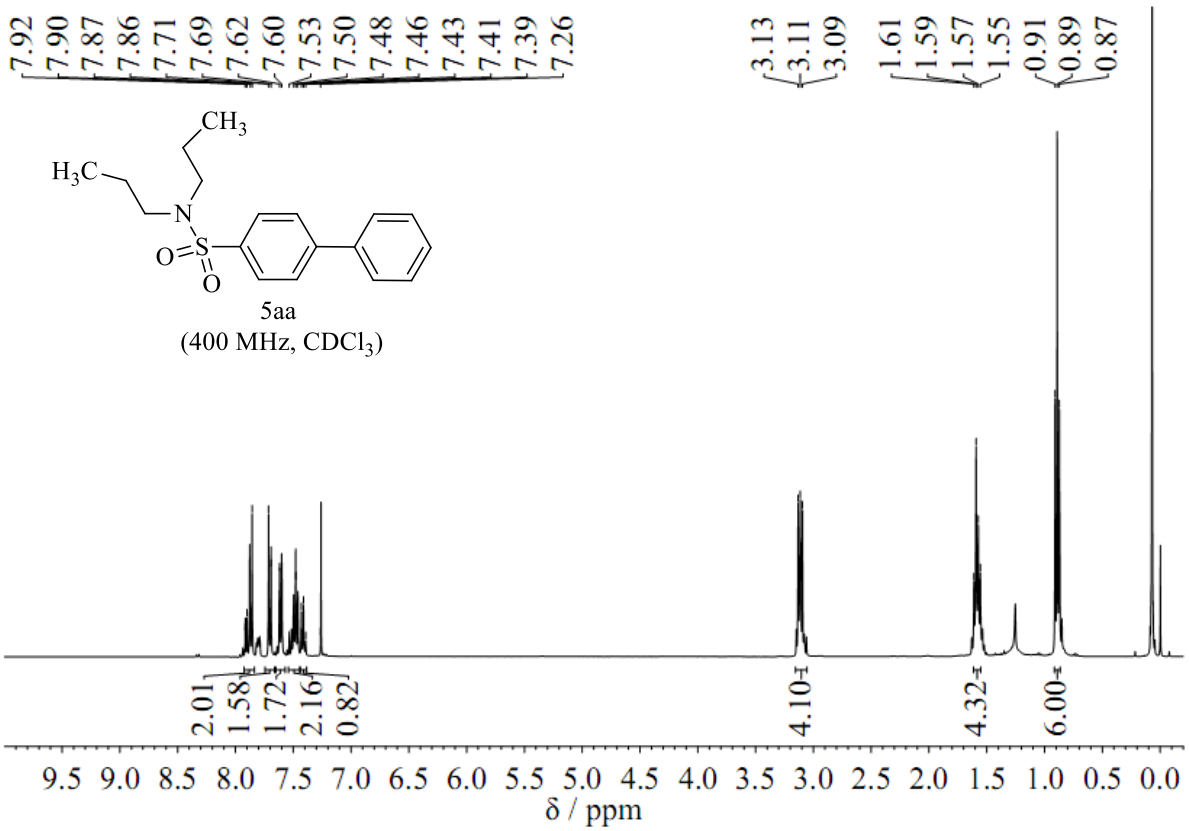

158.98
141.53
139.06
134.36
132.30
131.83
130.99
130.09
129.81
128.40
128.35
126.62
126.17
125.99
125.76
124.78
112.14
77.35
77.03
76.71
55.20
40.62
37.14
31.51
H3C
O
5y
(100 MHz, CDCl3)
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm



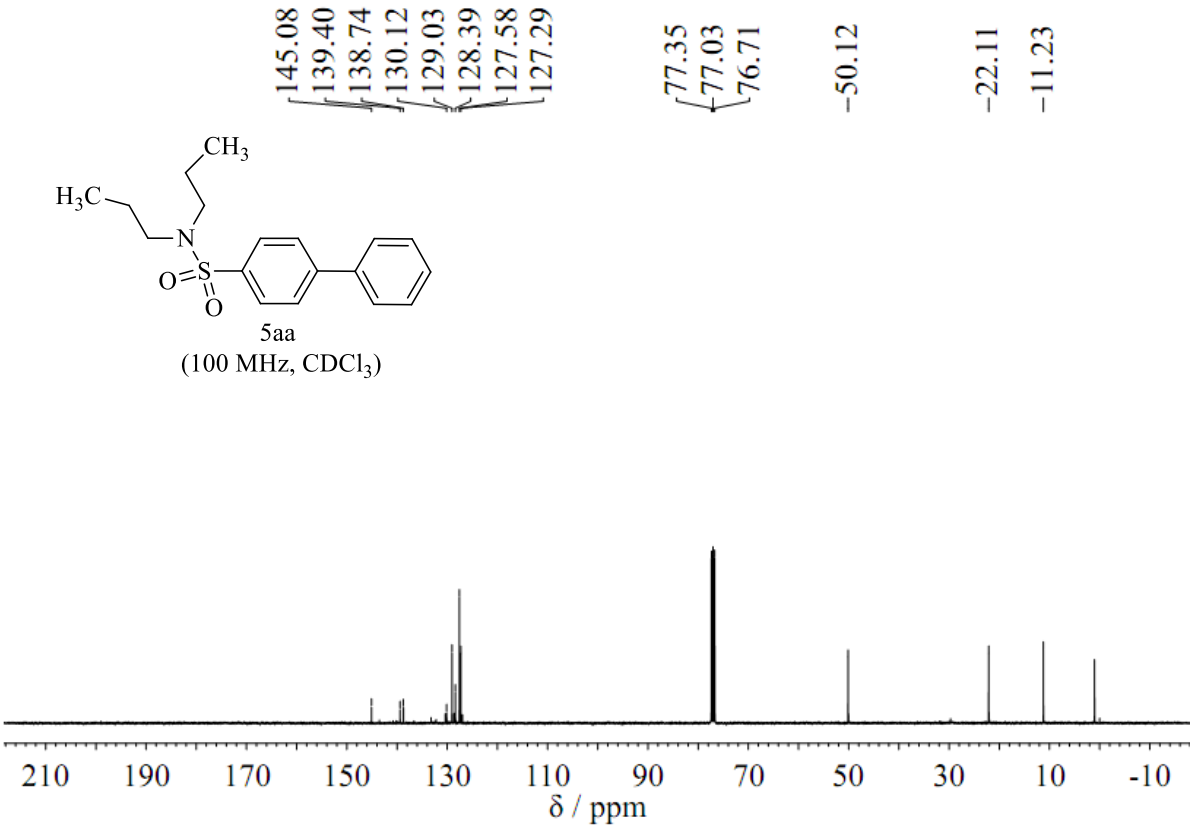
5z
(400 MHz, $CDCl_3$)



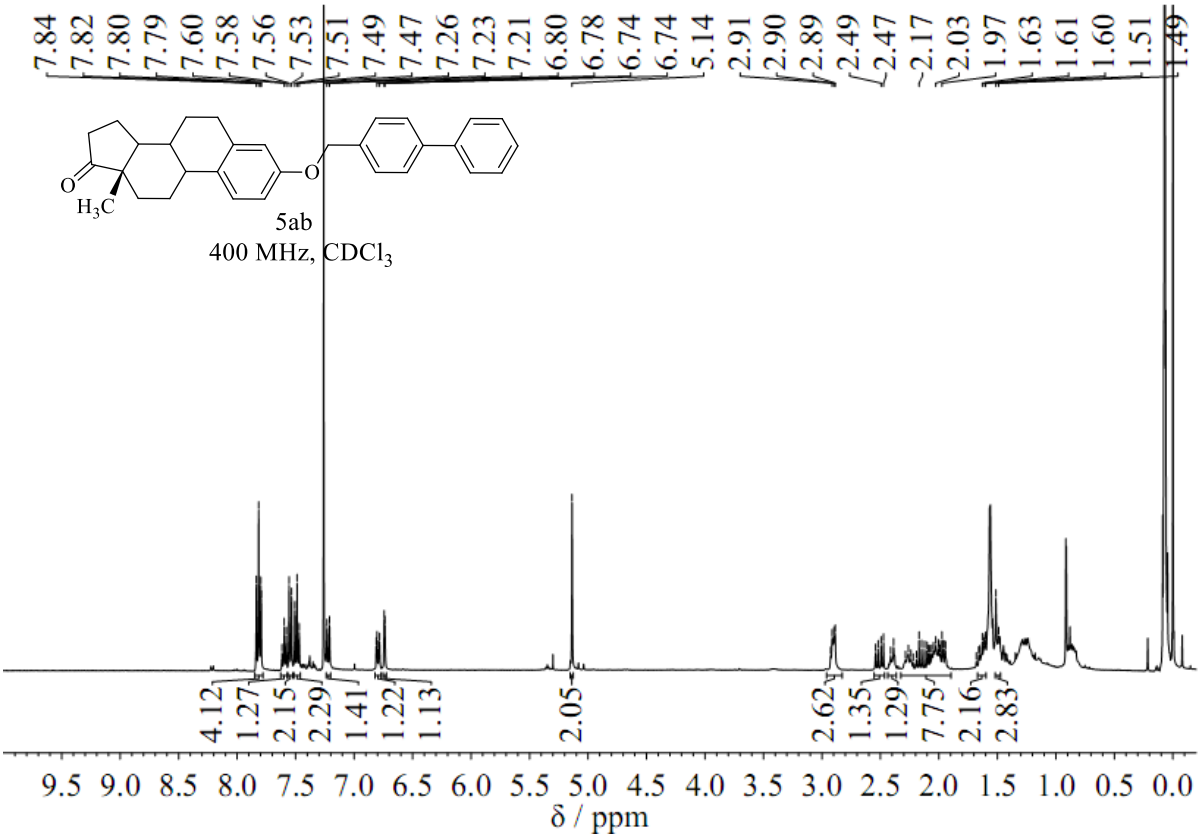
5z
(100 MHz, $CDCl_3$)

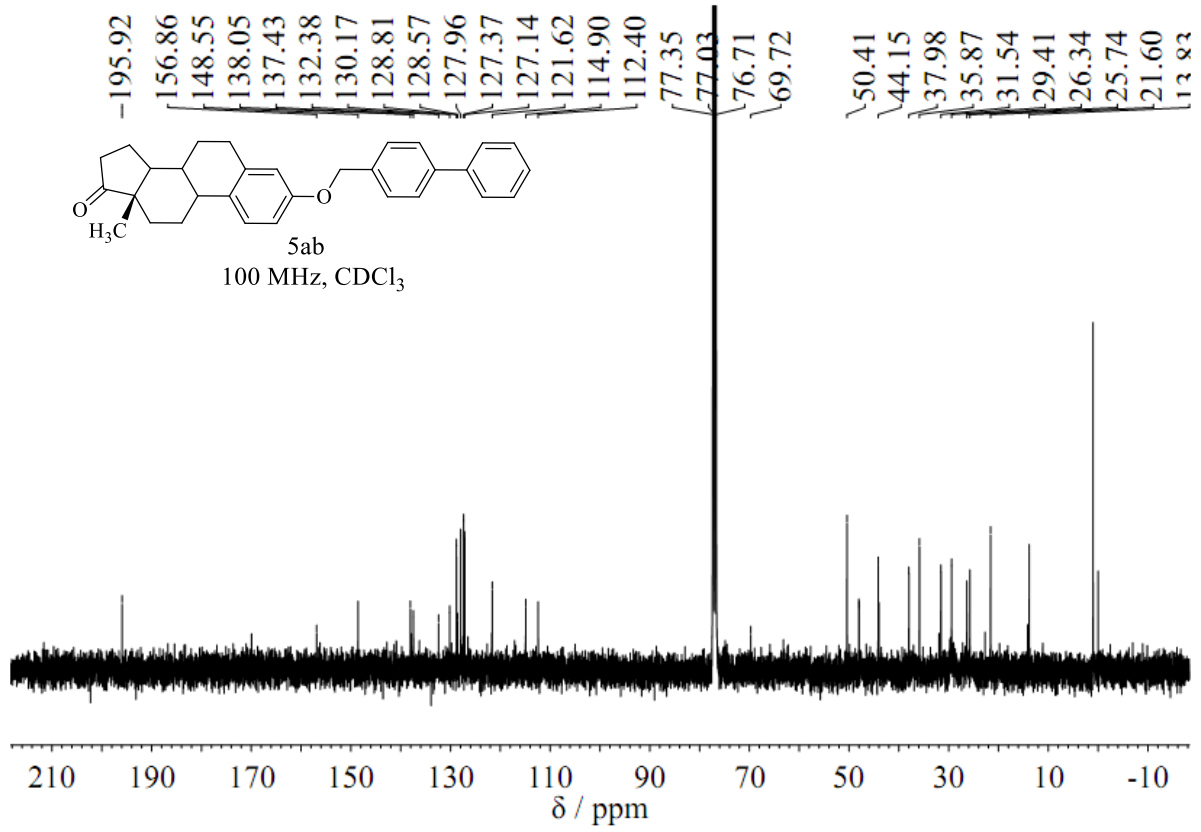


5aa
(400 MHz, $CDCl_3$)



5aa
(100 MHz, $CDCl_3$)


7.84 7.82 7.80 7.79 7.60 7.58 7.56 7.53 7.51 7.49 7.47 7.26 7.23 7.21 6.80 6.78 6.74 6.74 5.14 2.91 2.90 2.89 2.49 2.47 2.17 2.03 1.97 1.63 1.61 1.60 1.51 1.49
O
O
H3C
5ab
400 MHz, CDCl3
4.12 1.27 2.15 2.29 1.41 1.22 1.13 2.05 2.62 1.35 1.29 7.75 2.16 2.83
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
δ / ppm


195.92 156.86 148.55 138.05 137.43 132.38 130.17 128.81 128.57 127.96 127.37 127.14 121.62 114.90 112.40 77.35 77.03 76.71 69.72 50.41 44.15 37.98 35.87 31.54 29.41 26.34 25.74 21.60
O
O
H3C
5ab
100 MHz, CDCl3
210 190 170 150 130 110 90 70 50 30 10 -10
δ / ppm