Supplementary Material (ESI) for Chemical Communications


**ELECTRONIC SUPPORTING INFORMATION FOR**

# Terphenyl Crowns: A new family of Receptors Containing Ethereal Canopies that direct potassium cation onto benzenoid platforms for the cation-pi interactions

Ruchi Shukla, Sergey V. Lindeman, and Rajendra Rathore*

*Marquette University, Department of Chemistry, PO Box 1881, Milwaukee, WI 53201-1881*

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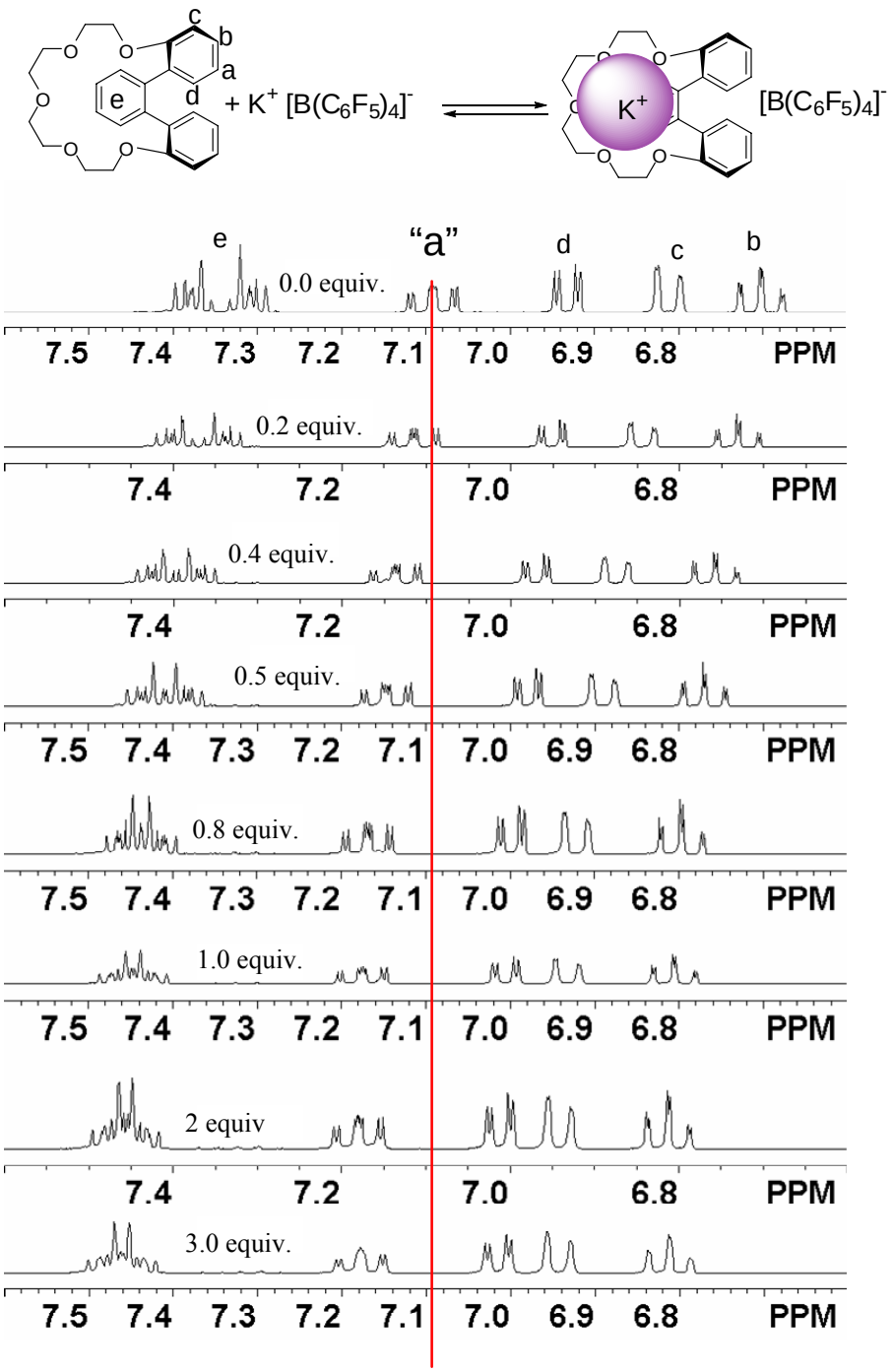



***Fig. S1A*** Partial $^{1}H$ spectra obtained upon incremental addition of $K^{+}$ $^{-}B(C_6F_5)_4$ (0.12 M) in acetone-*d6* to ***o*-TC** (0.03 M) in acetone-*d6* at 22°C. The assignments of the aromatic signals in ***o*-TC** is shown by letter "a"-"e" and the signal labeled "a" was chosen arbitrary for tracking of the $K^{+}$ binding.

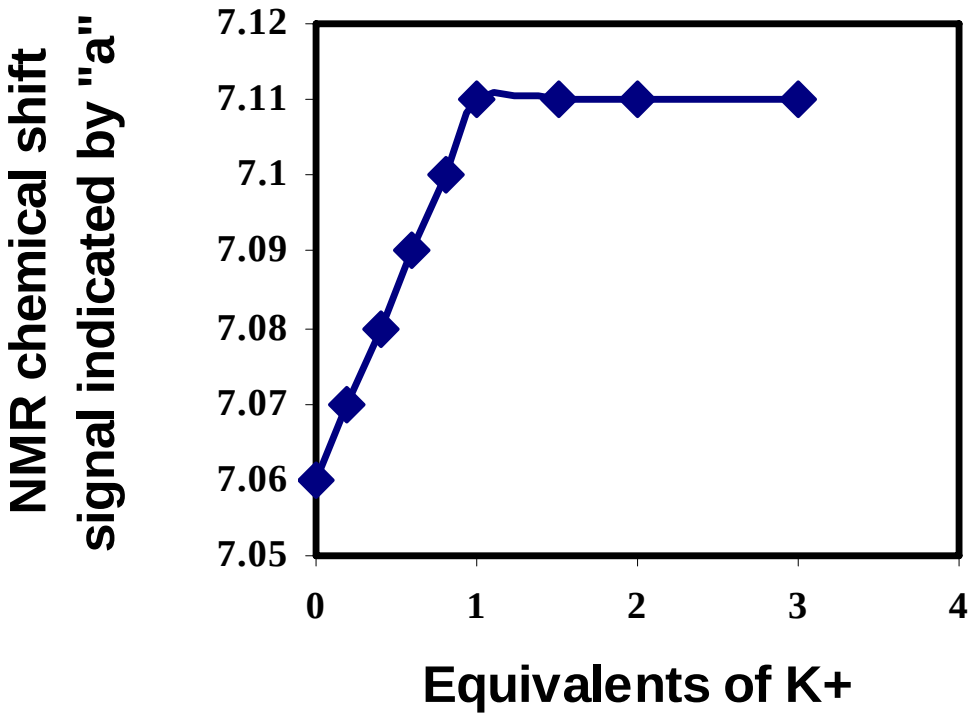



***Fig. S1B*** A plot of the changes in the chemical shift of one of the $^{1}$H NMR signals (identified by letter "a" in Figure S1A) upon the incremental addition of $KB(C_6F_5)_4$ to ***o-TC*** in acetone-$d_6$ at 22$^{o}$C.

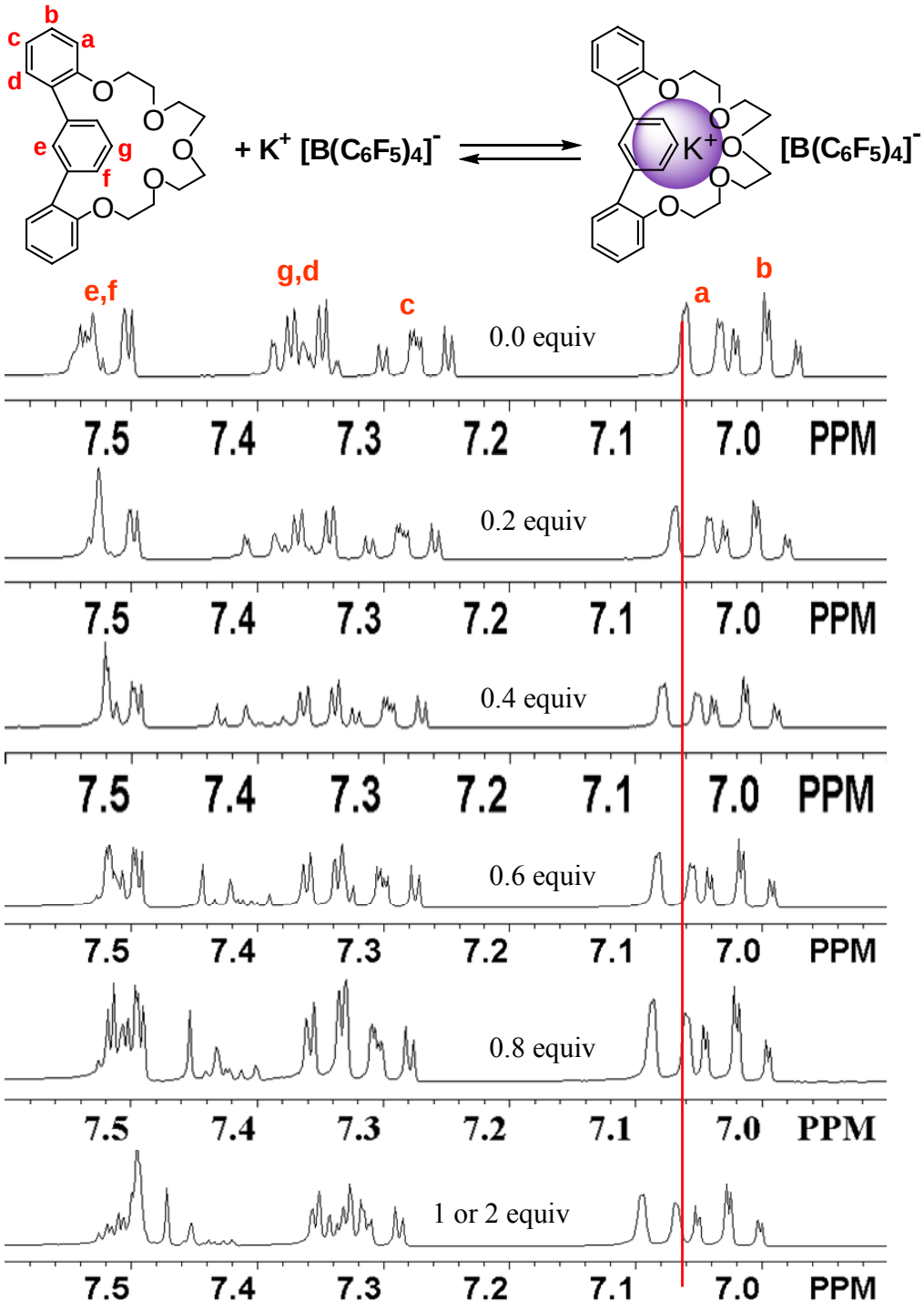



***Fig. S2A*** Partial $^{1}H$ spectra obtained upon incremental addition of $KB(C_6F_5)_4$ (0.12 M) in acetone-*d6* to ***m*-TC** (0.03 M) in acetone-*d6* at 22°C. The assignments of the aromatic signals in ***m*-TC** is shown by letter "a"-"g" and the signal labeled "a" was chosen arbitrary for tracking of the $K^+$ binding.

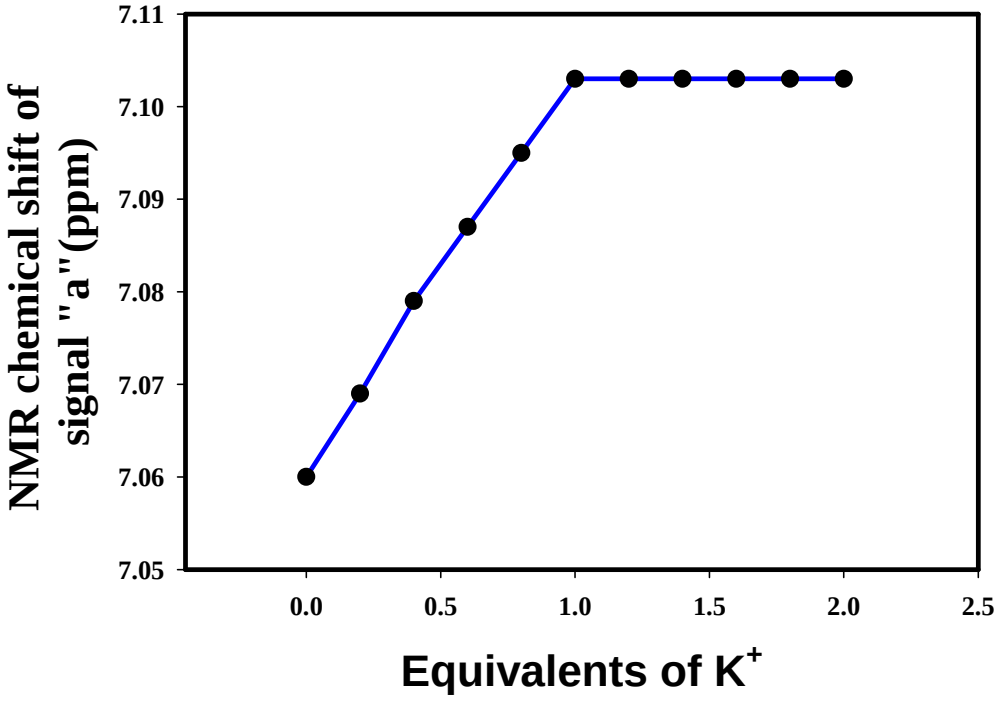



***Figure S2B.*** A plot of the changes in the chemical shift of one of the $^{1}$H NMR signals (identified by letter "a" in figure S2A) upon the incremental addition of $KB(C_6F_5)_4$ (0.12 M) in acetone-*d6* to ***m*-TC** (0.03 M) in acetone-*d6* at 22$^{o}$C

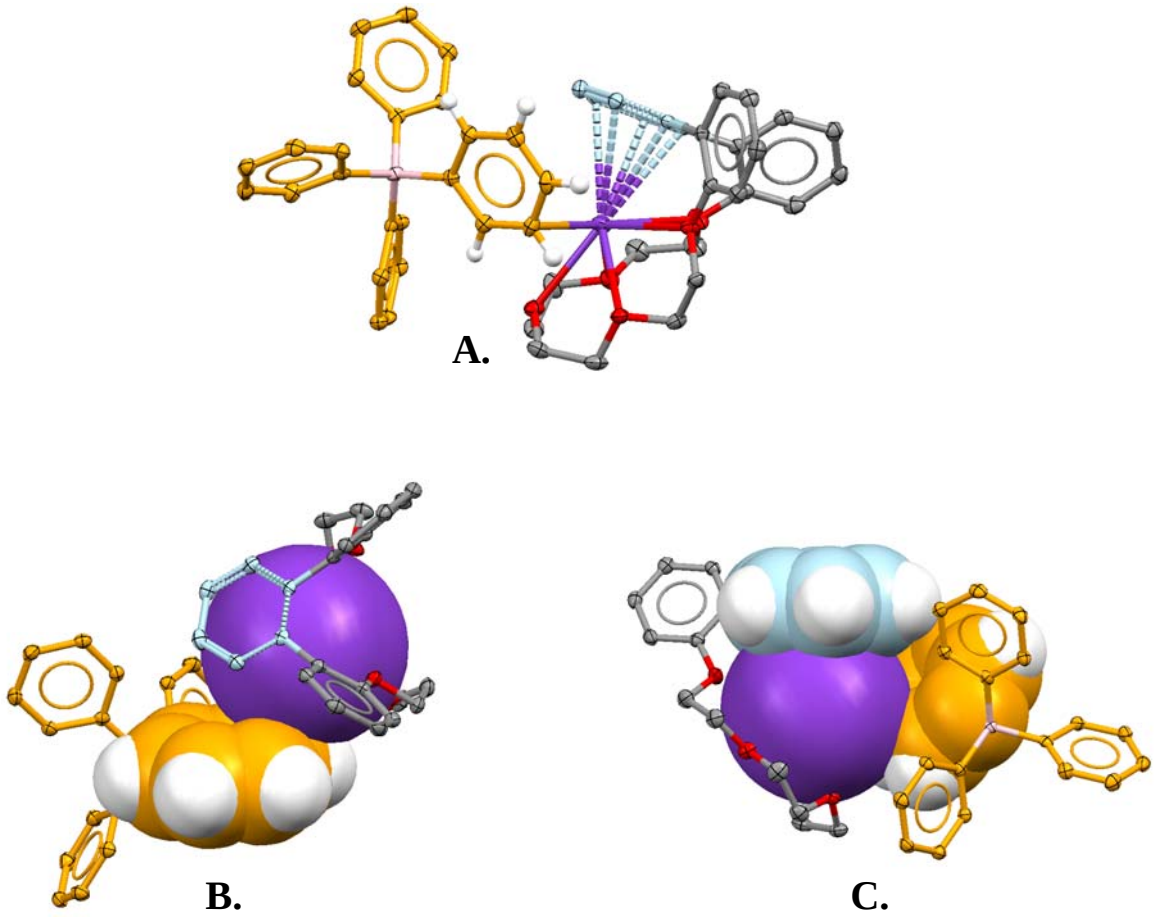



**Fig. S3** Different views of [***o*-TC**, $K^+$] $^-BPh_4$ complex showing that the ethereal canopy hold the $K^+$ onto the central aromatic ring while a single opening is protected by a phenyl group of the $^-BPh_4$ counter anion via cation-π interaction.

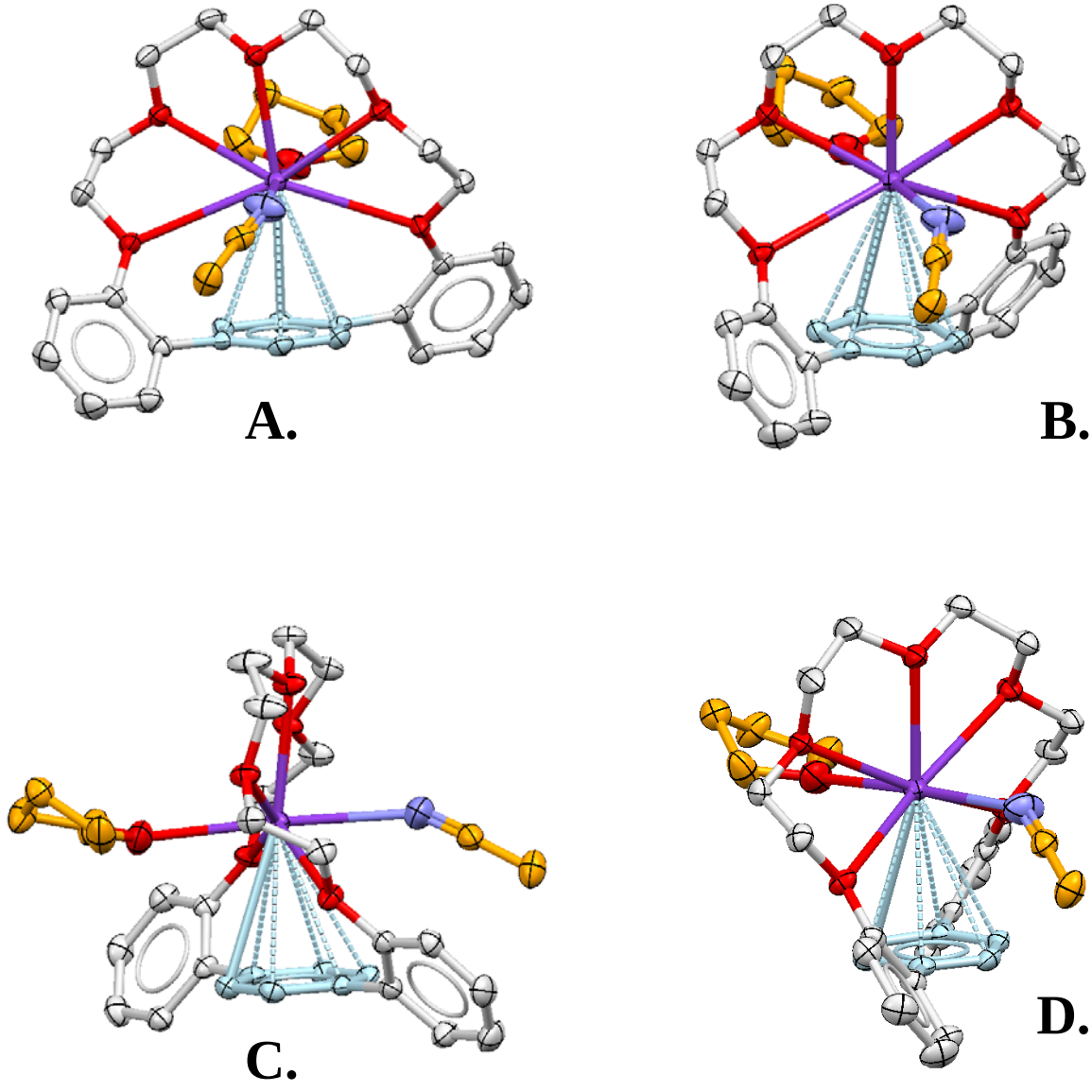



**Fig. S4** Different views of [***p*-TC**, $K^+$] showing that the ethereal canopy hold the $K^+$ onto the central aromatic ring while the two apical openings in the complex are plugged-in by solvent molecules (i.e. tetrahydrofuran and acetonitrile). The hydrogens are omitted for the sake of clarity.

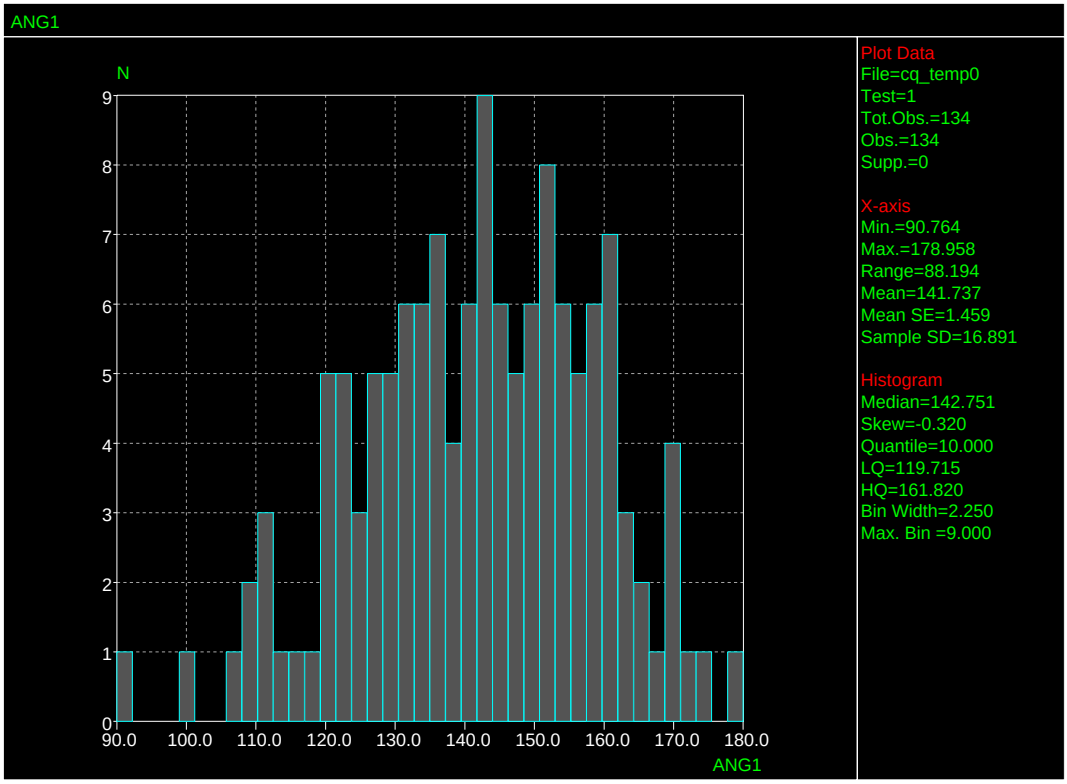



**Fig. S5** A histogram constructed from the angles of $K^+$...NC-R interactions using the X-ray structures data from the Cambridge Crystallographic database shows an average $K^+$···NC-R angle of ~140 deg. It is further noted that interaction of acetonitrile with $K^+$ is mostly an ion-dipole interaction and not a sigma-bond or a coordination bond. Therefore, the rigid bond angles from coordination chemistry are not applicable to this kind of bonding.

## General Experimental Methods

**NMR Spectroscopy.** All $^{1}H/^{13}C$ NMR spectra were recorded using a 300 MHz Varian NMR spectrometer using $CDCl_3$ as solvent unless otherwise noted.

**X-ray Crystallography.** X-ray diffraction intensities were collected at 100K (Oxford Cryostream 700 cooler) on a Bruker SMART diffractometer equipped with an APEX2 CCD detector using monochromatized $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å) or $CuK_\alpha$ radiation ($\lambda$ = 1.54178 Å) under APEX2 operational software (APEX2 v.2.0-2 Bruker-Nonius AXS, Madison, WI, 2005). The final unit cell dimensions were determined using as many as 10000 strongest reflections. The raw data integration and standard Lp corrections were performed with SAINT software (SAINT v.7.23A Bruker-Nonius AXS, Madison, WI, 2005). The data were corrected for absorption and related systematical errors using numerical absorption correction (based on real shape and composition of crystals) followed by SADABS program treatment (Sheldrick, G.M. SADABS-2004/1, Bruker-Nonius AXS, Madison, WI, 2004). The structures were solved with direct methods using SHELXS program (Sheldrick, G. M. XS/SHELXTL v.6.12, Bruker AXS, Madison, WI, 2001) and refined using full-matrix least-squares procedure with SHELXTL software (Sheldrick, G.M. SHELXTL-97, v.97-2, University of Göttingen, Germany, 1993-1997).

**Materials.** Potassium tetraphenylborate and potassium perfluorotetraphenylborate were commercially available and were used without further purification. Anhydrous tetrahydrofuran (THF) was prepared by refluxing the commercial tetrahydrofuran (Aldrich) over lithium tetrahydroaluminate under an argon atmosphere for 24 hours followed by

distillation. It was stored under an argon atmosphere in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from $P_2O_5$ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from $P_2O_5$ under an argon atmosphere and then refluxed over calcium hydride (~12 hrs). After distillation from $CaH_2$, the solvents were stored in Schlenk flasks under argon atmosphere.

***Preparation of 2-Methoxyphenylboronic acid***: A solution of 1-bromo-2-methoxybenzene (45 g, 240 mmol) in THF (200 mL) was added dropwise via a dropping funnel to a 500-mL Schlenk flask containing magnesium turnings (7.2 g, 300 mmol) in THF (20 mL). The reaction was refluxed for 3 h, and then cooled to room temperature. The resulting Grignard reagent was added dropwise with stirring to a pre-chilled (-78 $^{o}$C) solution of trimethyl borate (36 mL, 320 mmol) in THF (200 mL) at such a rate that the temperature did not rise above -70 °C. The suspension was stirred and allowed to warm to room temperature during a course of 12 h. The reaction mixture was then poured onto ice (300 g) and concentrated sulfuric acid (7.0 mL) and the resulting mixture was stirred for 30 min and then extracted with ether (3 x 150 mL). The combined organic extracts were dried over anhydrous magnesium sulfate and evaporated under reduced pressure to afford 2-methoxyphenylboronic acid as a white powder. Yield: 31.0 g (80 %); $^{1}$H NMR ($CDCl_3$) δ:

3.85 (s, 3H), 6.70 (s, 2H), 6.85 (d, 1H), 7.00 (br t, 1H), 7.40 (br t, 1H), 7.85 (d, 1H); $^{13}$C NMR (CDCl3): 55.65, 110.13, 121.44, 133.04, 137.05, 164.68.

***2,2'-Dimethoxy-ortho-terphenyl (o-1). General Procedure:*** A solution of 2-methoxyphenylboronic acid (3.6 g, 23.8 mmol) and 1,2-diiodobenzene (3.28 g, 9.94 mmol) in DME (50 mL) in a schlenk flask was sequentially evacuated and filled with argon (3x). To this mixture a catalytic amount of *tetrakis*(triphenylphosphine)palladium (0.2 g, 0.17 mmol) and an aqueous (degassed) solution of sodium carbonate (2 M, 130 mL) was added successively and the resulting mixture was refluxed for 16 h. After cooling to room temperature, the reaction mixture was poured into water (250 mL) and extracted with dichloromethane (3 x 50 mL). The organic layers were combined, dried over magnesium sulfate and evaporated under reduced pressure. The resulting crude material was purified by column chromatography over silica gel using 90:10 mixture of hexanes/ethyl acetate as an eluent to afford pure ***o*-1** as a colorless solid.

Using the general procedure described above, ***m*-1** and ***p*-1** were similarly prepared in excellent yields and the spectral data are summarized below:

***o*-1:** Yield: 89%; mp 98-100 $^{o}$C; $^{1}$H NMR ($CDCl_3$) δ: 3.45 (s, 6H), 6.68 (d, 2H), 6.80 (t, 2H), 7.06 (d, 2H), 7.12 (dt, 2H), 7.38 (s, 4H); $^{13}$C NMR ($CDCl_3$) δ: 55.05, 110.31, 119.93, 127.24, 128.20, 130.64, 131.07, 131.55, 138.50, 156.33; GC-MS: *m/z* = 290 ($M^+$) calcd for $C_{20}H_{18}O_2$.

***m*-1:** Yield: 92%; mp 92-94 $^{o}$C ; $^{1}$H NMR ($CDCl_3$): 3.78 (s, 6H), 6.96 (d, 2H), 7.01 (t, 2H) ), 7.30 (dt, 2H) ), 7.37 (dd, 2H); ), 7.39-7.54 (m, 3H), 7.69 (br s, 1H); $^{13}$C NMR ($CDCl_3$): 55.69, 111.33, 120.98, 127.73, 128.39, 128.73, 130.94, 130.96, 131.19, 138.33, 156.69; GC-MS: *m/z* = 290 ($M^+$) calcd for $C_{20}H_{18}O_2$.

***p*-1:** 90%; mp 195-197 $^{o}$C ; $^{1}$H NMR ($CDCl_3$) δ: 3.87 (s, 6H), 7.03 (d, 2H), 7.08 (dt, 2H), 7.36 (dt, 2H) ), 7.43 (dd, 2H), 7.63 (s, 4H); $^{13}$C NMR ($CDCl_3$) δ: 55.73, 111.35, 121.03, 128.74, 129.36, 130.66, 131.11, 137.24, 156.74; GC-MS: *m/z* = 290 ($M^+$) calcd for $C_{20}H_{18}O_2$.

***2,2'-Dihydroxy-o-terphenyl (o-2). General Procedure.*** Neat $BBr_3$ (3.0 g, 12.0 mmol) was added slowly to a pre-chilled (–78 $^{o}$C) solution of 2,2'-dimethoxy-*o*-terphenyl (2.8 g, 9.7 mmol) in dichloromethane (100 mL) under an argon atmosphere. The resulting mixture was stirred and allowed to warm to room temperature during a course of 12 h and was then quenched by a slow addition of water (5 mL). The reaction mixture was then transferred into a separatory funnel containing 100 mL water. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). Combined organic extracts were dried over anhydrous magnesium sulfate and evaporated under reduced pressure to afford dihydroxy derivative ***o*-2** in quantitative yield, and it was used in the next step without additional purification. Using the general procedure described above, ***m*-2** and ***p*-2** were similarly prepared and the spectral data are summarized below:

***o*-2:** Yield: 98%; mp 148-150 $^{o}$C, $^{1}$H NMR ($CDCl_3$) δ: 5.58 (br s, 2H), 6.63 (d, 2H), 6.76 (dt, 2H), 6.96 (dd, 2H), 7.03 (dt, 2H), 7.42 (d, 4H); $^{13}$C NMR ($CDCl_3$) δ: 115.71, 120.50, 127.76, 128.56, 129.03, 131.08, 131.42, 137.36, 152.44. GC-MS: *m/z* = 262 (M+) calcd for $C_{18}H_{14}O_2$.

***m*-2:** mp 108-110 °C; $^{1}$H NMR ($CDCl_3$) δ: 5.37 (s, 2H), 6.89 (d, 2H), 6.97 (dt, 2H), 7.22 (m, 2H), 7.44 (m, 3H), 7.61 (br s, 1H); $^{13}$C NMR ($CDCl_3$) δ: 116.25, 121.22, 128.06, 128.48, 129.39, 129.87, 130.19, 130.57, 138.11, 152.49. GC-MS: *m/z* = 262 ($M^+$) calcd for $C_{18}H_{14}O_2$.

***p*-2:** mp 176-178 $^{o}$C ; $^{1}$H NMR ($CDCl_3$) δ: 5.24, (s, 2H), 7.02 (m, 4H) ), 7.29 (m, 4H), 7.61 (s, 4H); $^{13}$C NMR ($CDCl_3$) δ: 116.23, 121.28, 127.79, 129.55, 130.11, 130.57, 136.91, 152.69; GC-MS: *m/z* = 262 ($M^+$) calcd for $C_{18}H_{14}O_2$.

***Ortho-terphenyl crown ether (o-TC). General Procedure.*** Potassium hydride (1.52 g, 38 mmol) was suspended in anhydrous THF (50 mL) and cooled in an ice bath. To this mixture a solution of 2,2'-dihydroxy-*o*-terphenyl (2.4 g, 9.2 mmol) in THF (25 mL) was added via a dropping funnel and it was stirred for an additional 10 min. To this mixture was added a solution of tetraethyleneglycol-*p*-ditosylate (4.6 g, 9.2 mmol) in THF (75 mL) via a dropping funnel. After addition was complete, the cooling bath was removed and the reaction mixture was refluxed for 18 h. After which time, it was cooled to 22 $^{o}$C and quenched with water (100 mL). The aqueous layer was extracted with dichloromethane (3 x 50 mL) and the combined organic extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to afford a cream-colored sticky solid which was purified by column chromatography on silica gel using mixture of hexanes/ethyl acetate as eluent. The resulting material was recrystallized from a mixture of dichloromethane and acetonitrile to afford ***o*-TC** as a colorless solid. Using the general procedure described above, ***m*-TC** and ***p*-TC** were similarly prepared and the spectral data are summarized below:

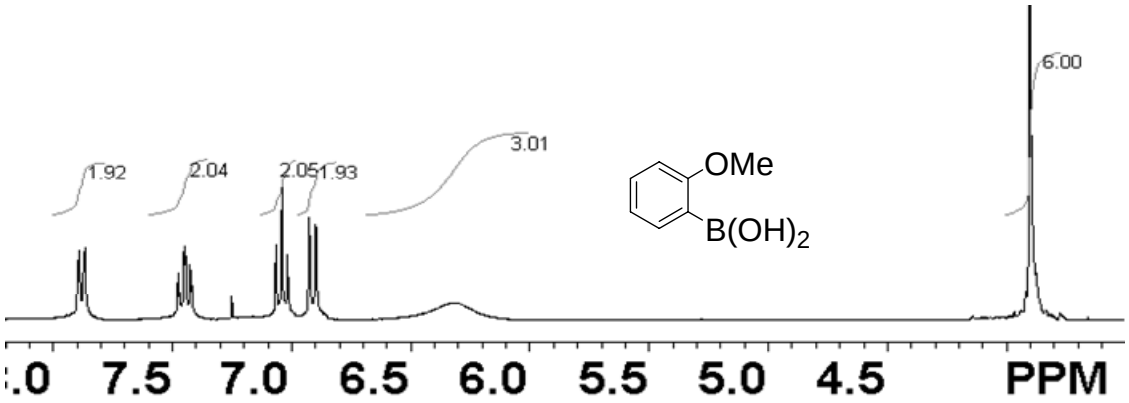
***o*-TC:** Yield: 75%; mp 92-94 °C; $^{1}$H NMR ($CDCl_3$) δ: 3.35 (m, 4H), 3.45 (m, 4H), 3.55-3.90 (m, 8H), 6.65 (m, 4H), 6.90 (d, 2H), 7.30 (m, 2H), 7.40 (m, 3H), 7.56 (m, 3H); $^{13}$C NMR ($CDCl_3$) δ: 68.70, 70.16, 70.59, 111.70, 120.08, 126.58, 128.20, 130.91, 131.06, 131.76, 138.17, 155.62. GC-MS: *m/z* = 420 ($M^+$) calcd for $C_{26}H_{28}O_5$.

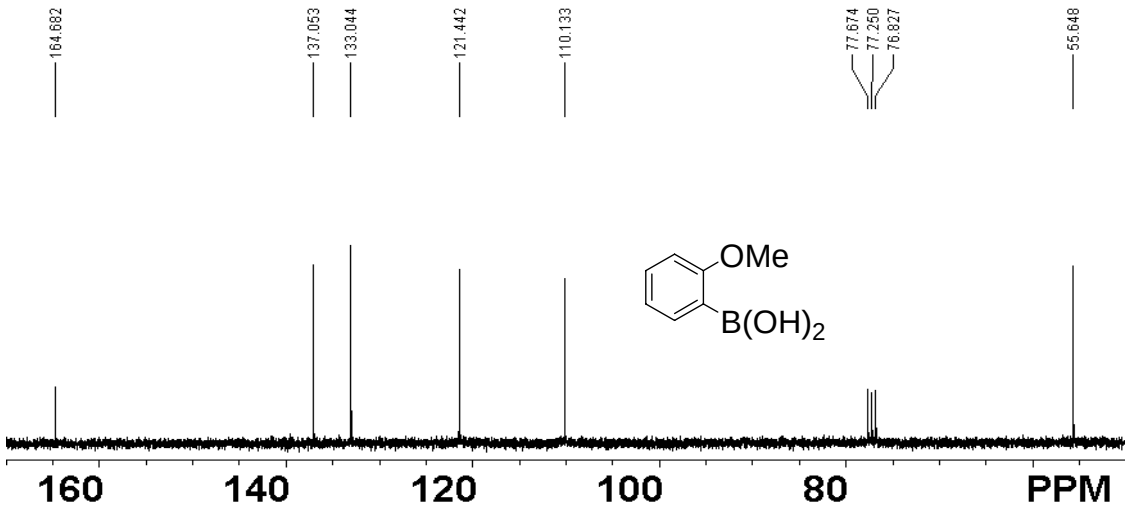
***m*-TC:** Yield: 70%; mp 73–75 °C; $^{1}$H NMR ($CDCl_3$) δ: 3.45 (m, 8H), 3.80 (m, 4H), 4.12 (m, 4H), 6.96 (d, 2H), 7.04 (dt, 2H), 7.30 (m, 2H), 7.40 (m, 3H), 7.56 (m, 3H); $^{13}$C NMR

($CDCl_3$) δ: 69.09, 69.57, 69.98, 71.98, 112.33, 121.15, 126.92, 128.69, 128.75, 130.58, 131.24, 131.37, 138.71, 156.00. GC-MS: *m/z* = 420 ($M^+$) calcd for $C_{26}H_{28}O_5$.

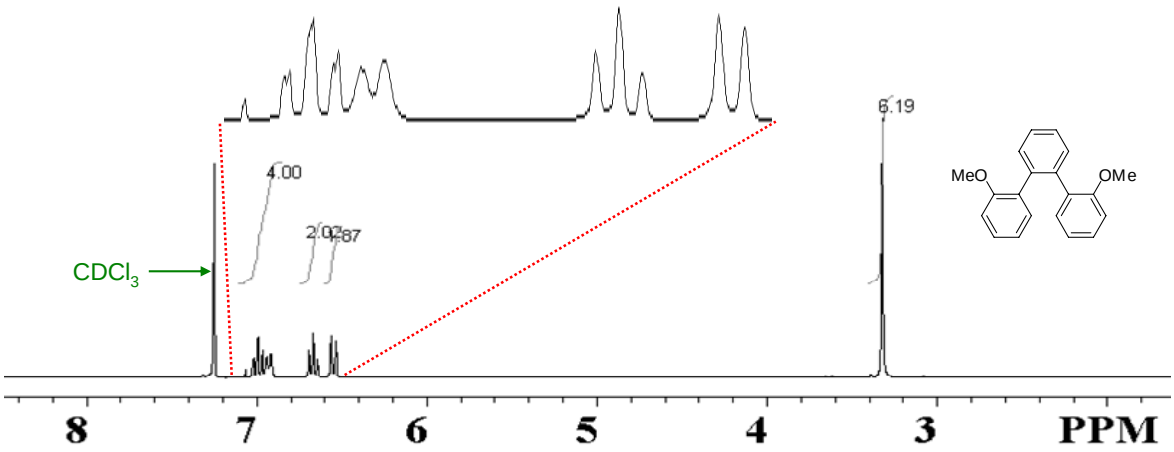
***p*-TC:** Yield: 74%; mp 142-144 °C; $^1H$ NMR ($CDCl_3$) δ: 3.68 (s, 8H), 3.80 (m, 4H), 4.20 (m, 4H), 6.94 (d, 2H), 7.06 (t, 2H), 7.31 (dt, 2H), 7.46 (dd, 2H), 7.83 (s, 4H); $^{13}C$ NMR ($CDCl_3$) δ: 67.92, 69.79, 71.07, 71.46, 111.70, 120.99, 128.47, 129.54, 130.47, 130.76, 136.81, 156.01. GC-MS: *m/z* = 420 ($M^+$) calcd for $C_{26}H_{28}O_5$.

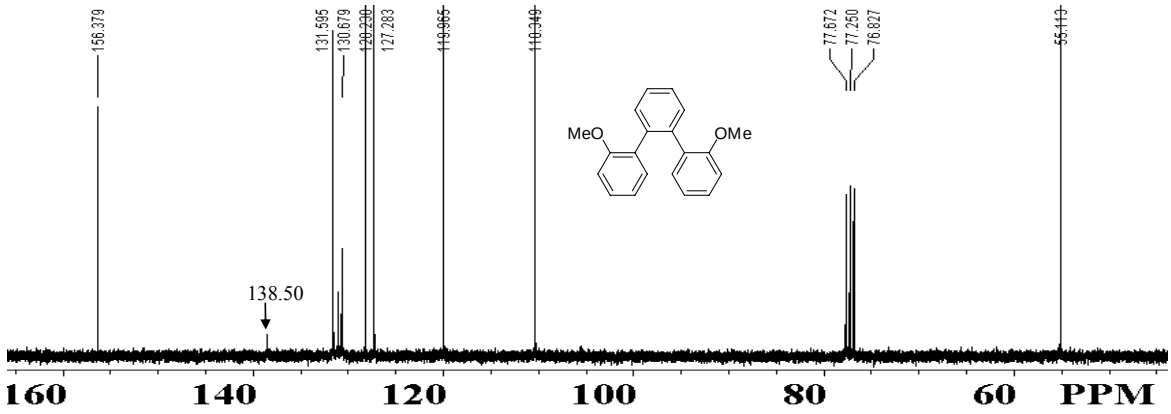
## $^{1}H$ and $^{13}C$ NMR spectra of 2-Methoxyphenylboronic acid



## $^{1}H$ and $^{13}C$ NMR spectra of 2,2'-Dimethoxy-*o*-terphenyl (*o*-1)



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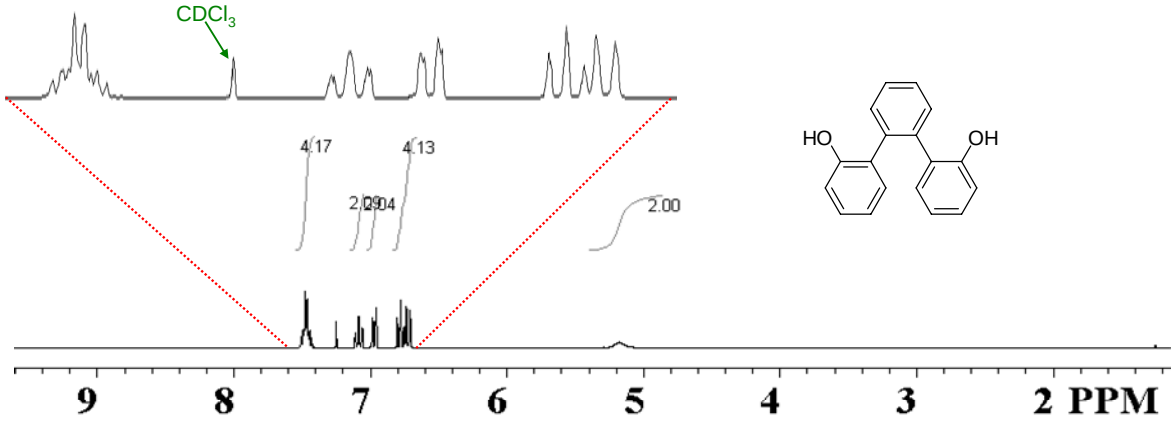


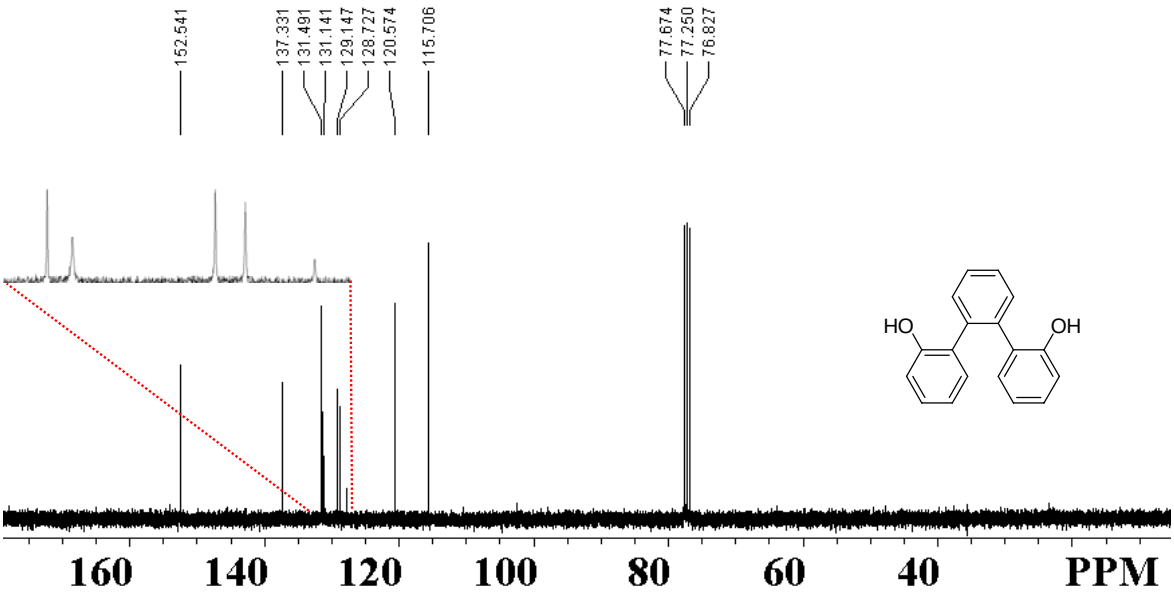

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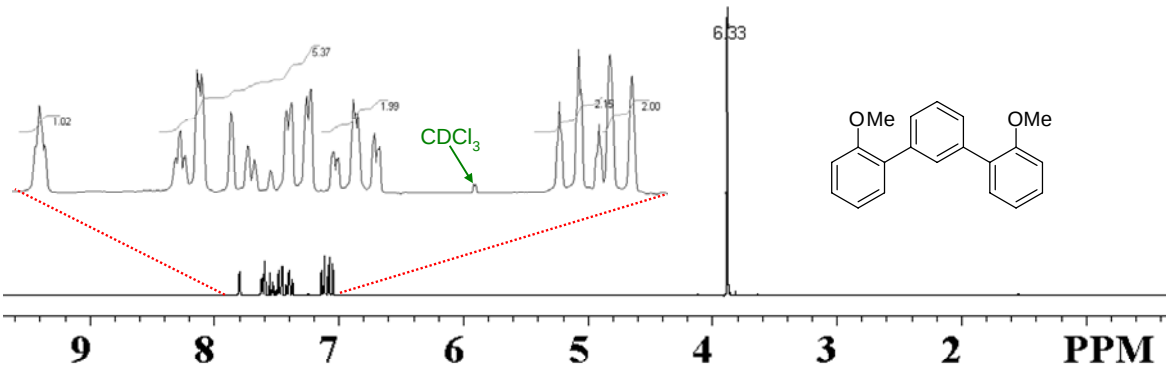


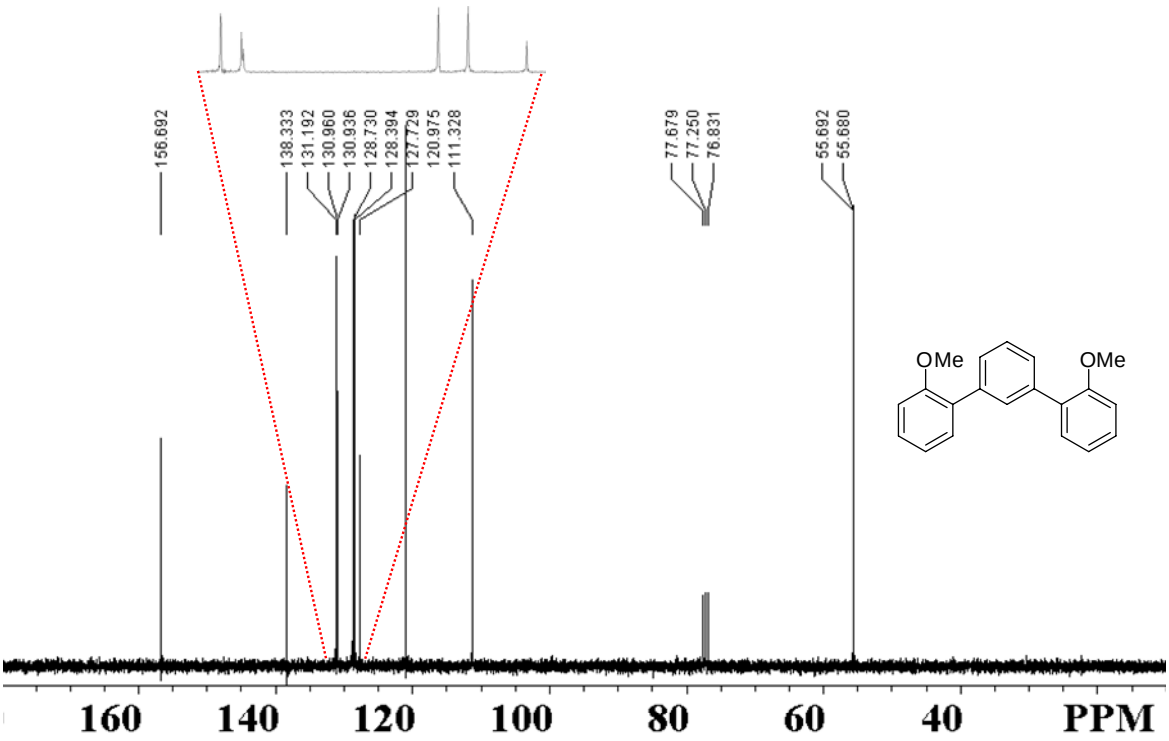

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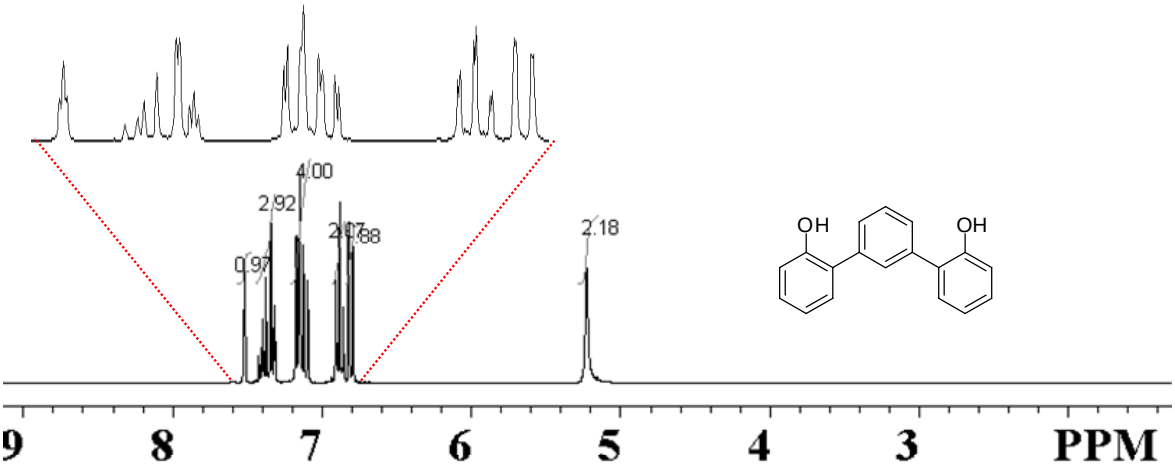
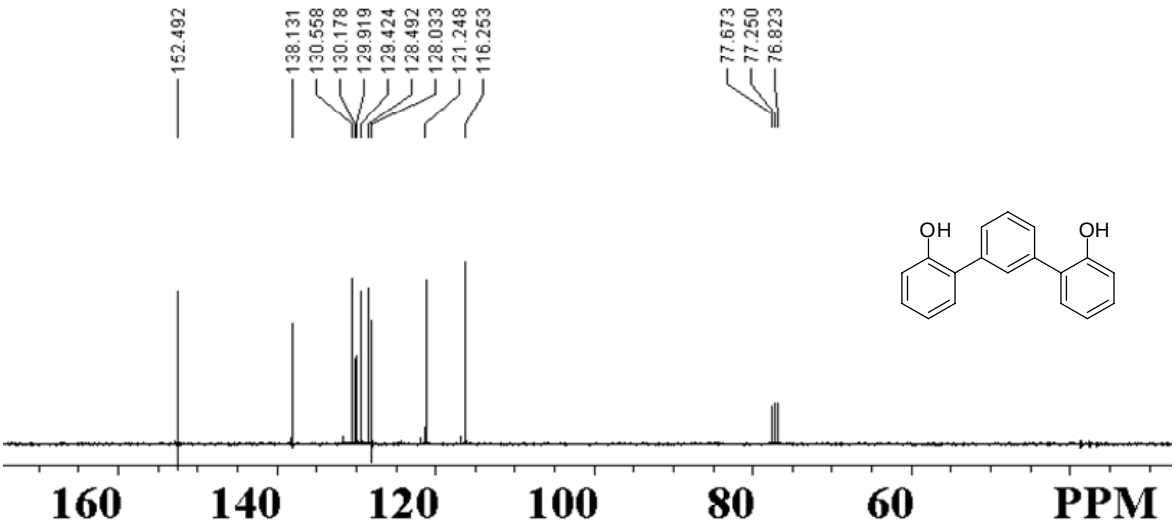
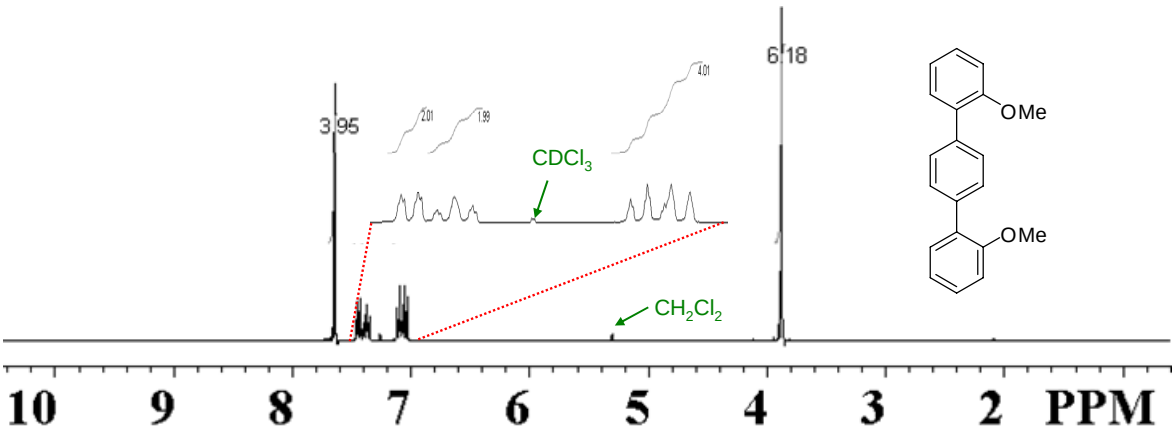
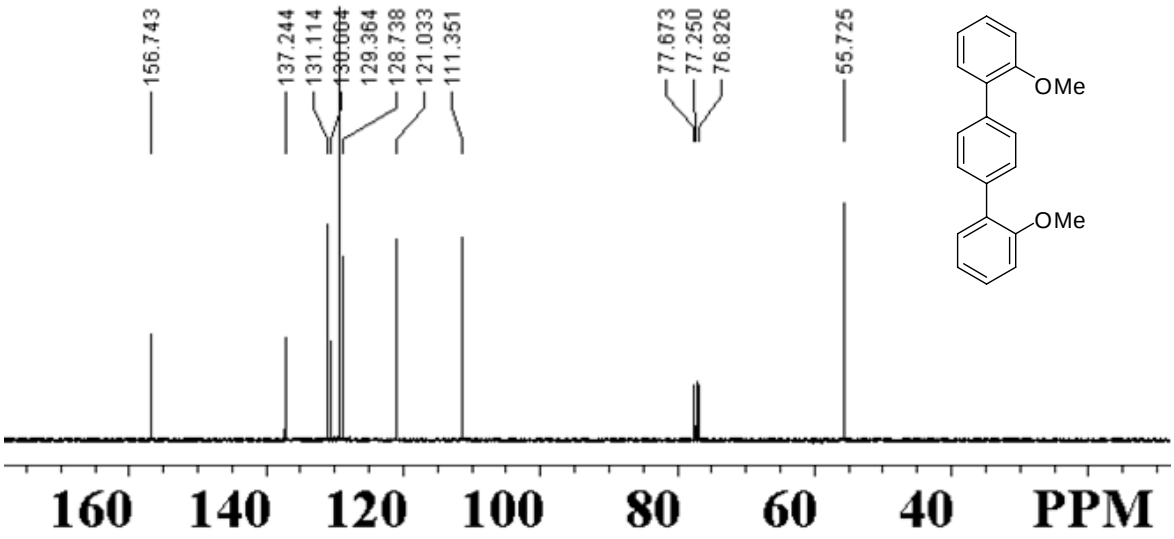


## $^{1}$H and $^{13}$C NMR spectra of 2,2'-Dimethoxy-*p*-terphenyl (*p*-1)



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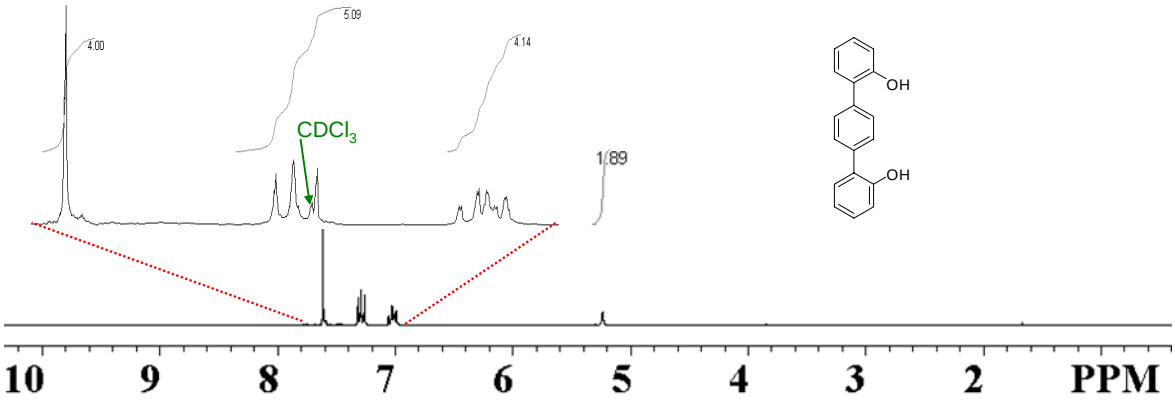
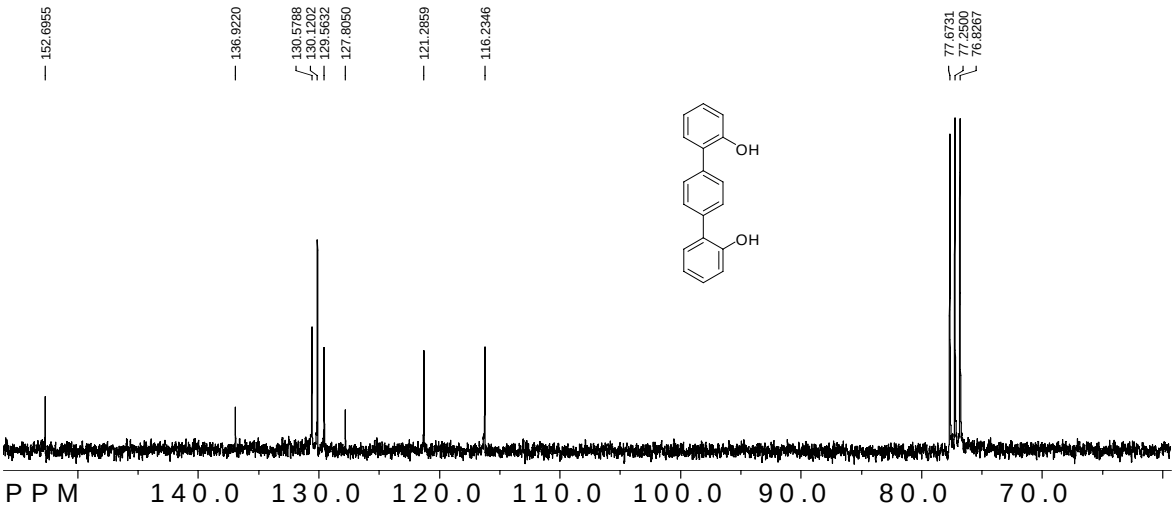
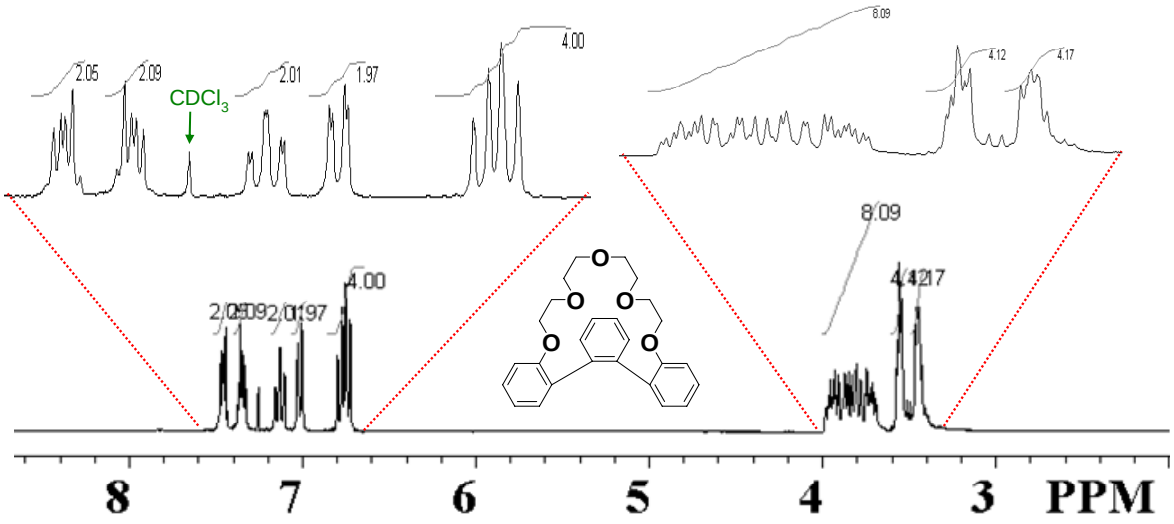
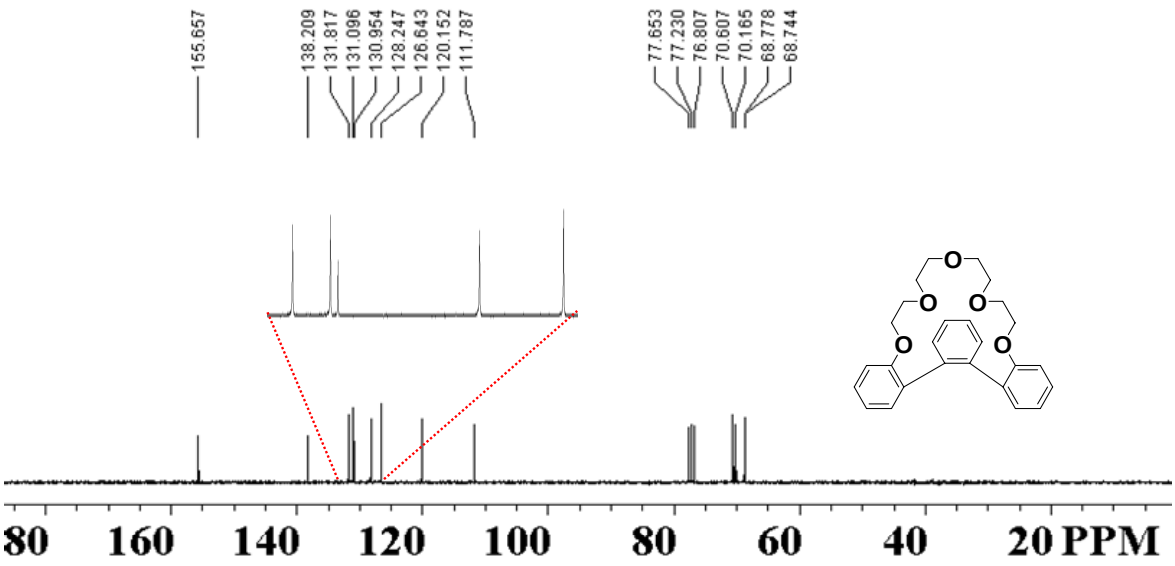


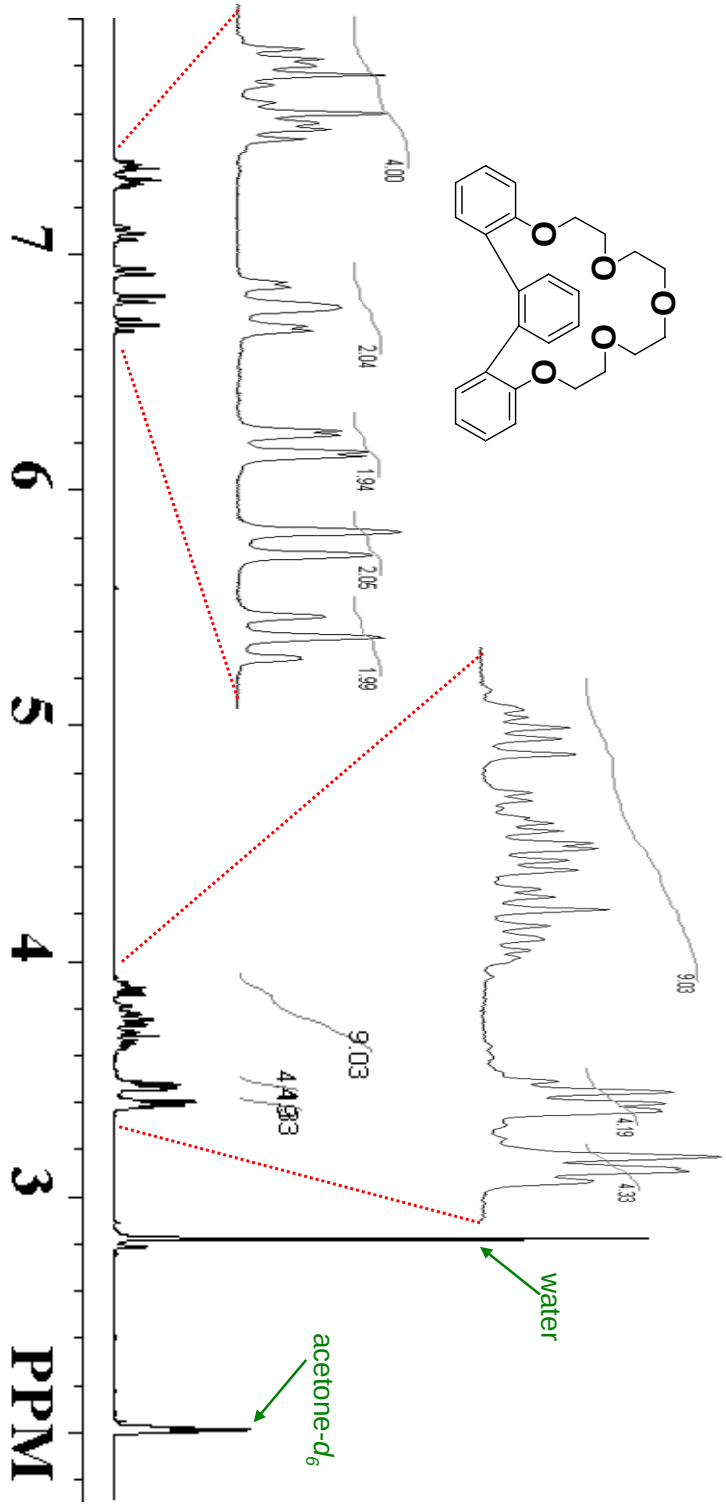



## $^{1}$H and $^{13}$C NMR spectra of *ortho*-terphenyl crown ether (*o*-TC) in $CDCl_3$

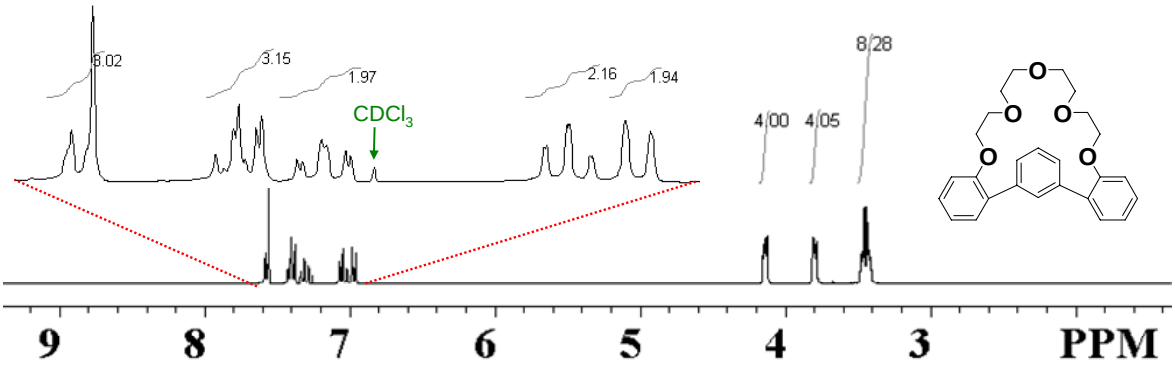


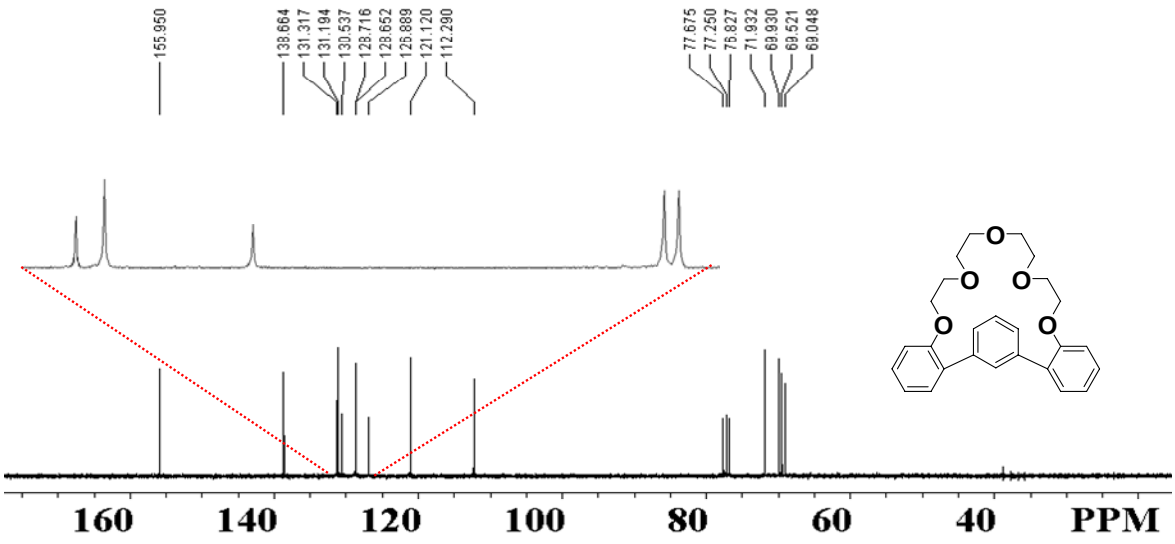



**$^1$H NMR spectrum of *ortho*-terphenyl crown ether (*o*-TC) in acetone-$d_6$**

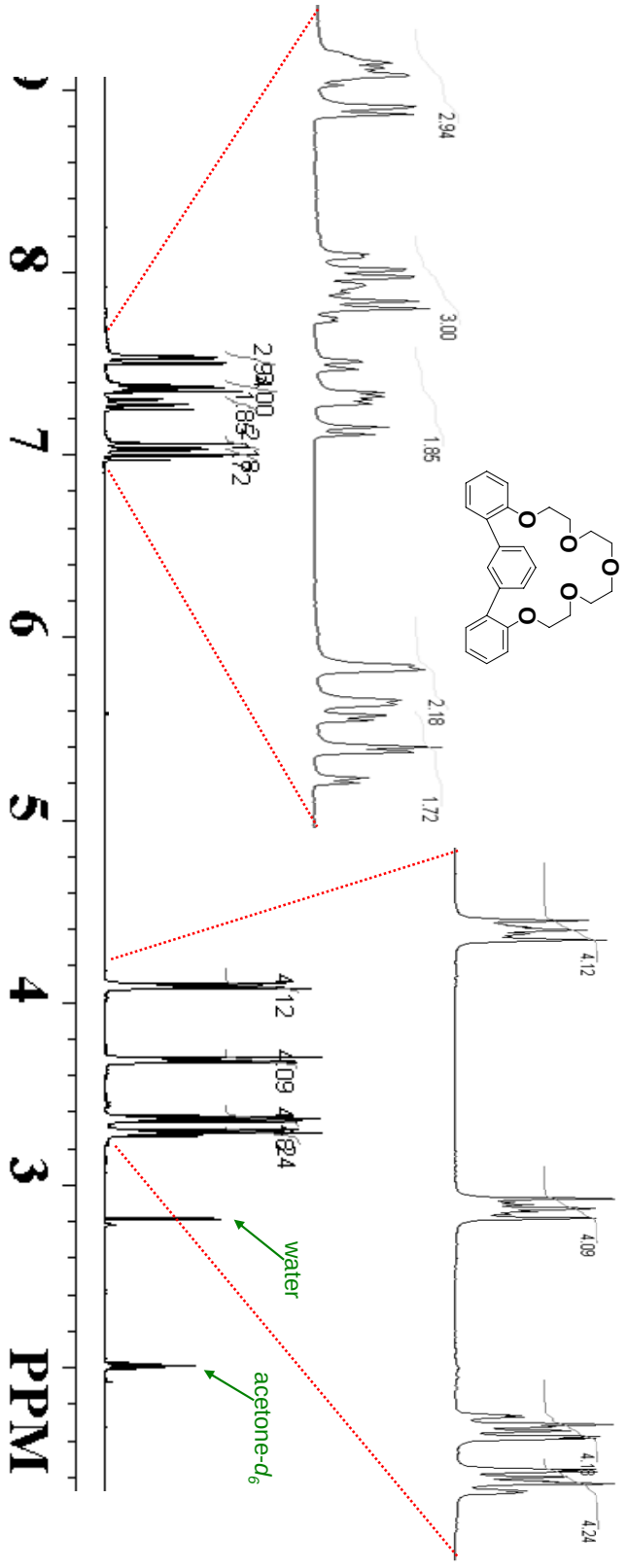


## $^{1}$H and $^{13}$C NMR spectra of *meta*-terphenyl crown ether (*m*-TC)

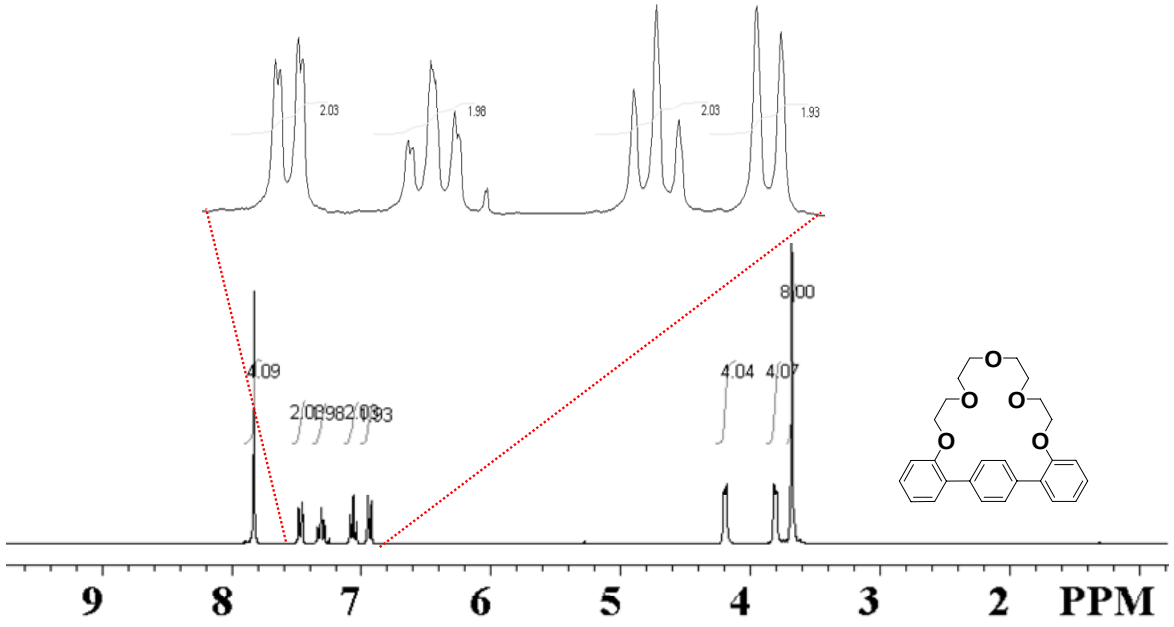


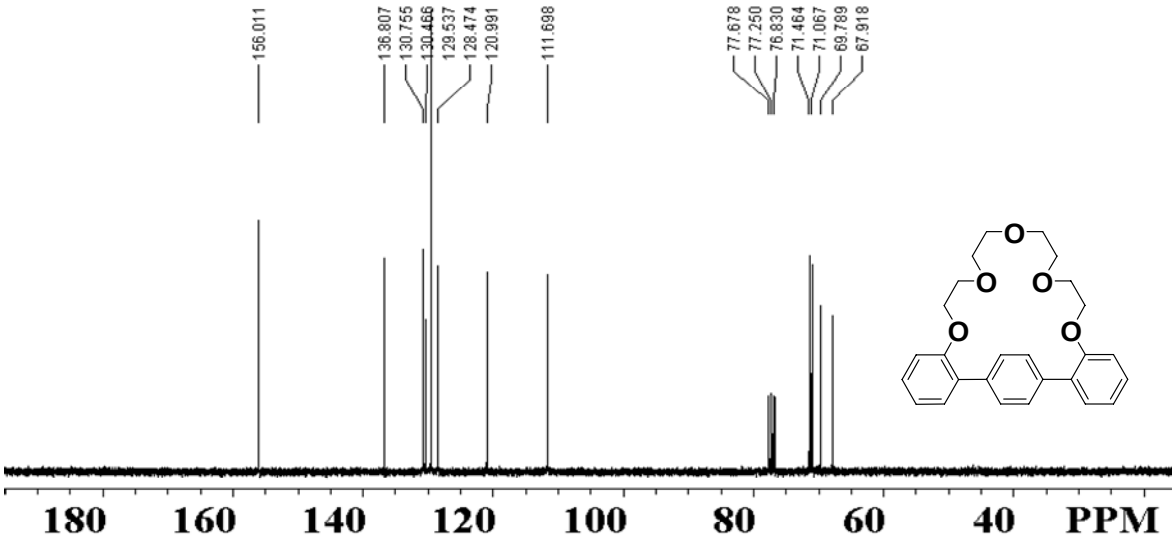



**$^1$H NMR spectrum of *meta*-terphenyl crown ether (*m*-TC) in acetone-$d_6$**



## $^{1}$H and $^{13}$C NMR spectra of *para*-terphenyl crown ether (*p*-TC)



**$^1$H NMR spectrum of *para*-terphenyl crown ether (*p*-TC) in acetone-$d_6$**