Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# "Supramolecular buttressing effects" in Cucurbit[7]uril/guest assemblies

Roymon Joseph and Eric Masson*

*Department of Chemistry and Biochemistry, Ohio University, Athens, OH 45701, USA*

*e-mail: masson@ohio.edu*

## Supporting Information

## 1. $^{1}$H and $^{13}$C NMR characterization of biphenyls 1 – 5

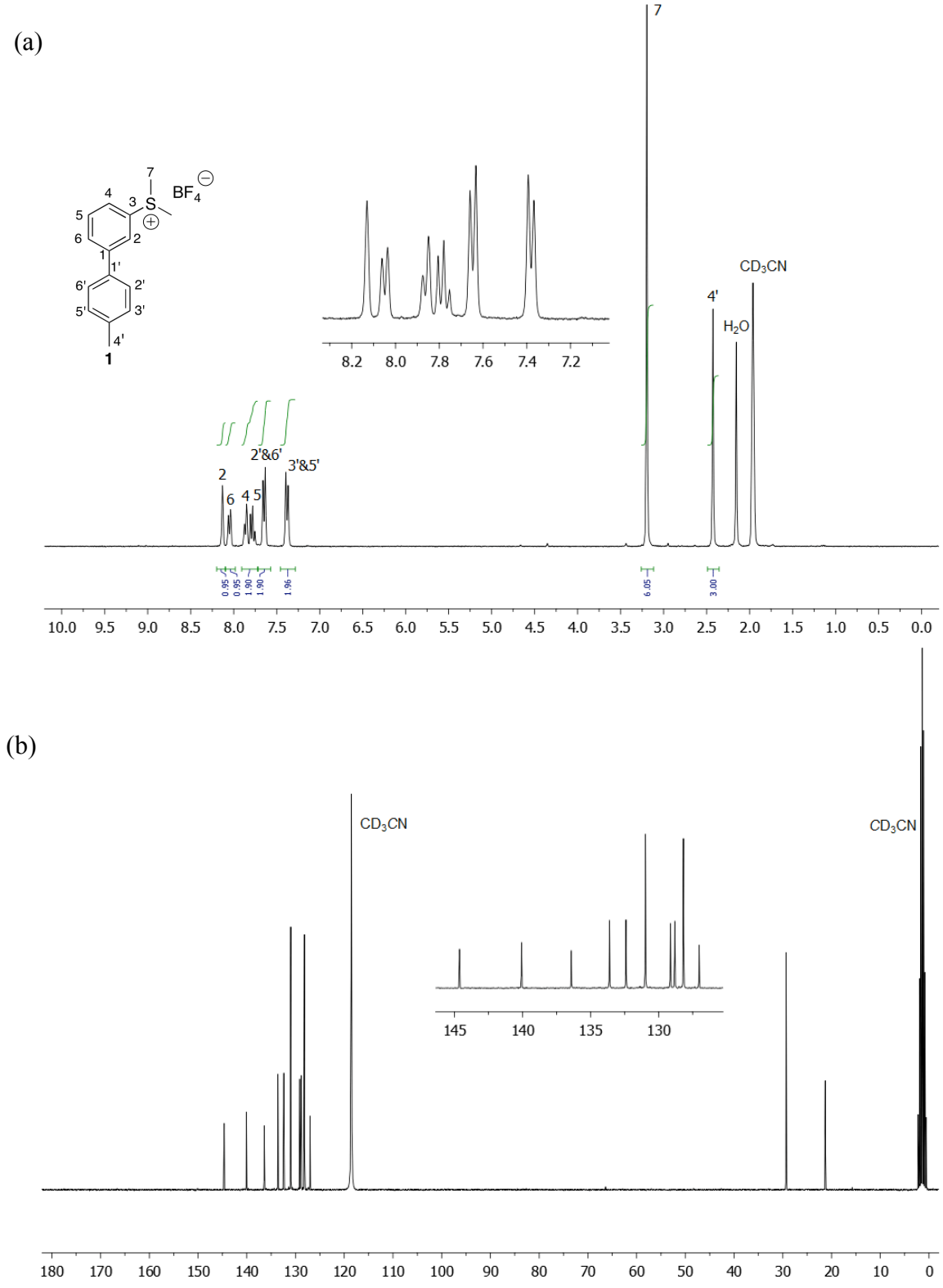


**Figure 1.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of biphenyl **1** in $CD_3CN$.

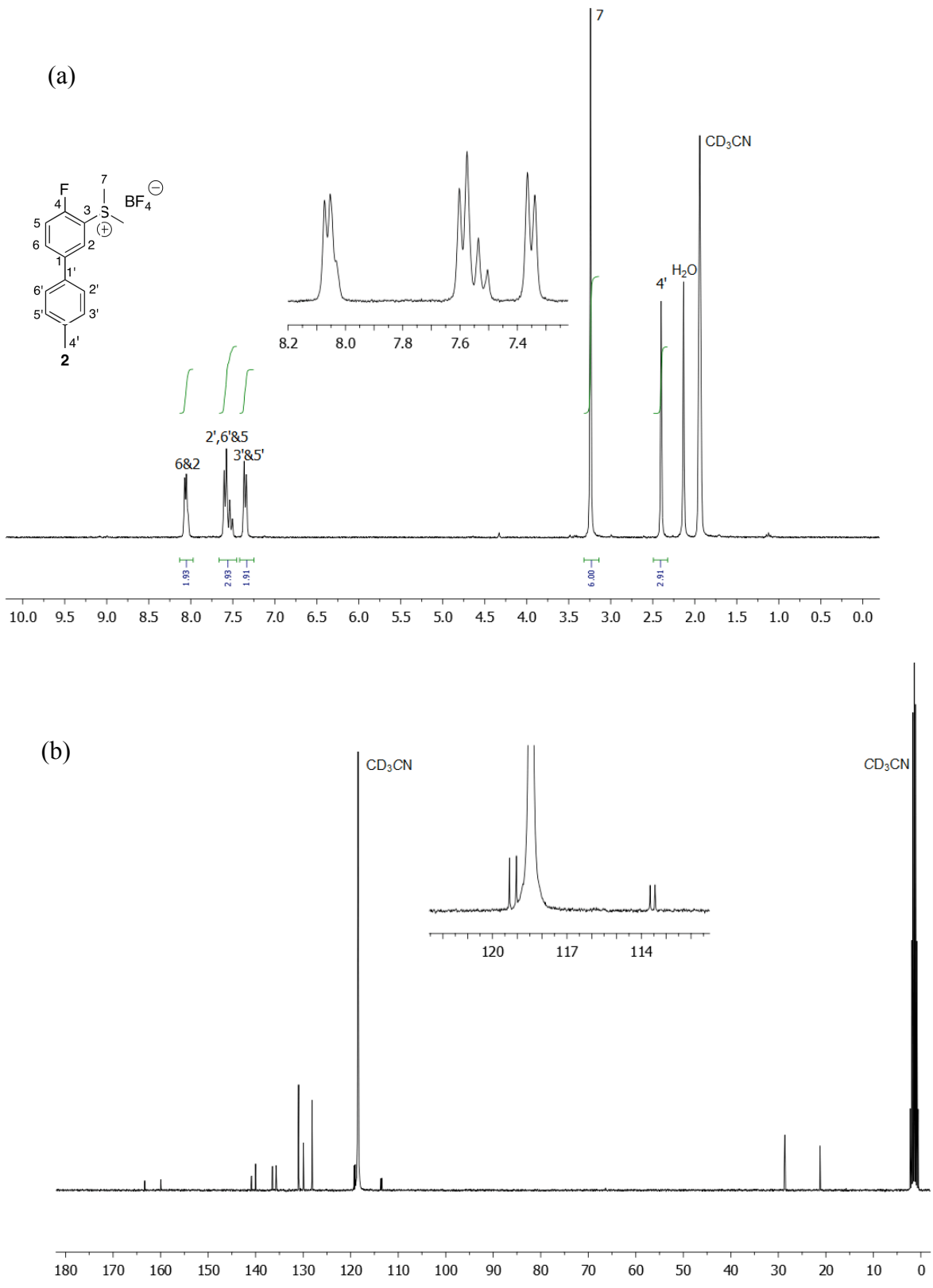


**Figure 2.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of biphenyl **2** in $CD_3CN$.

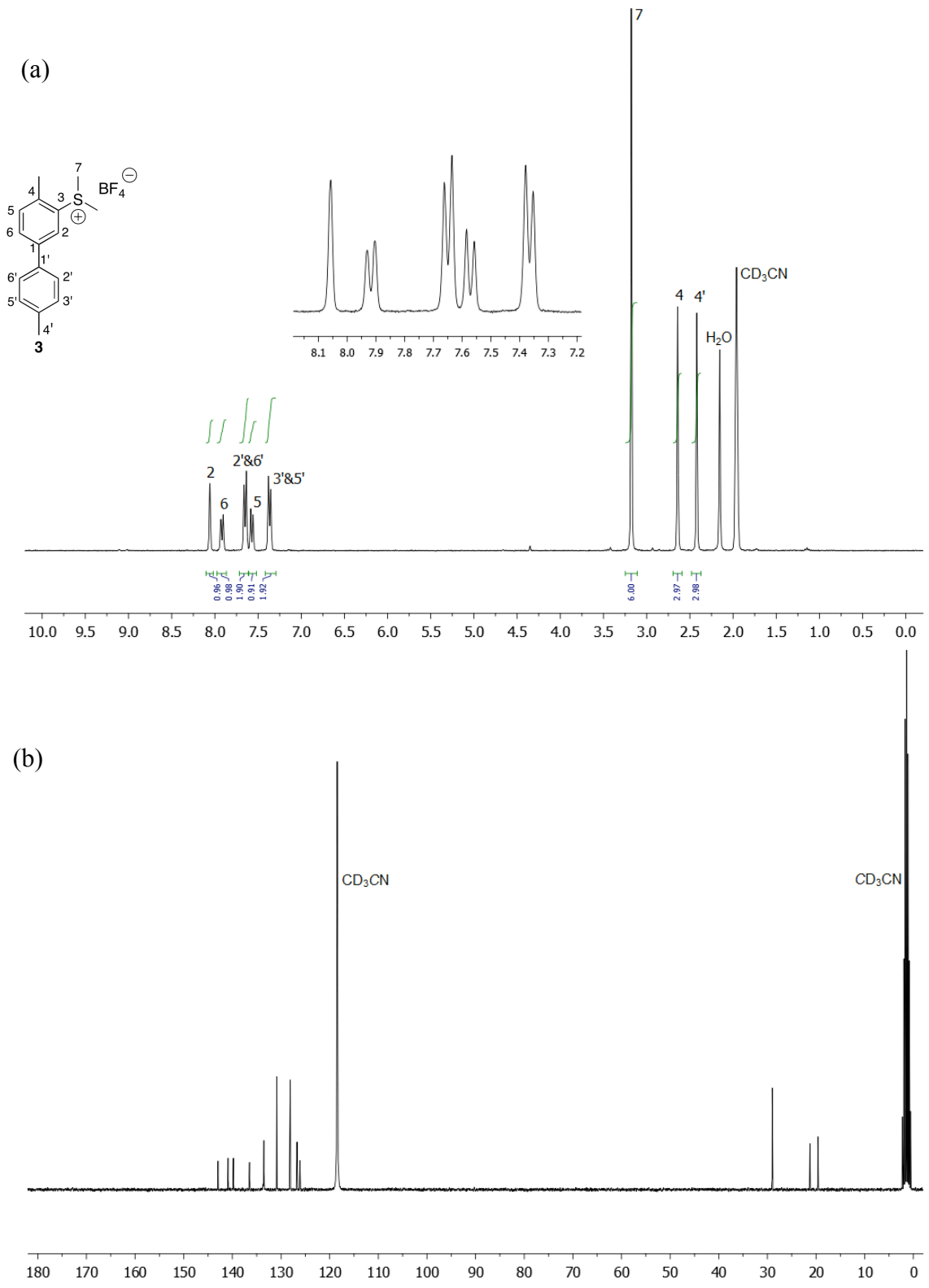


**Figure 3**. (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of biphenyl **3** in $CD_3CN$.

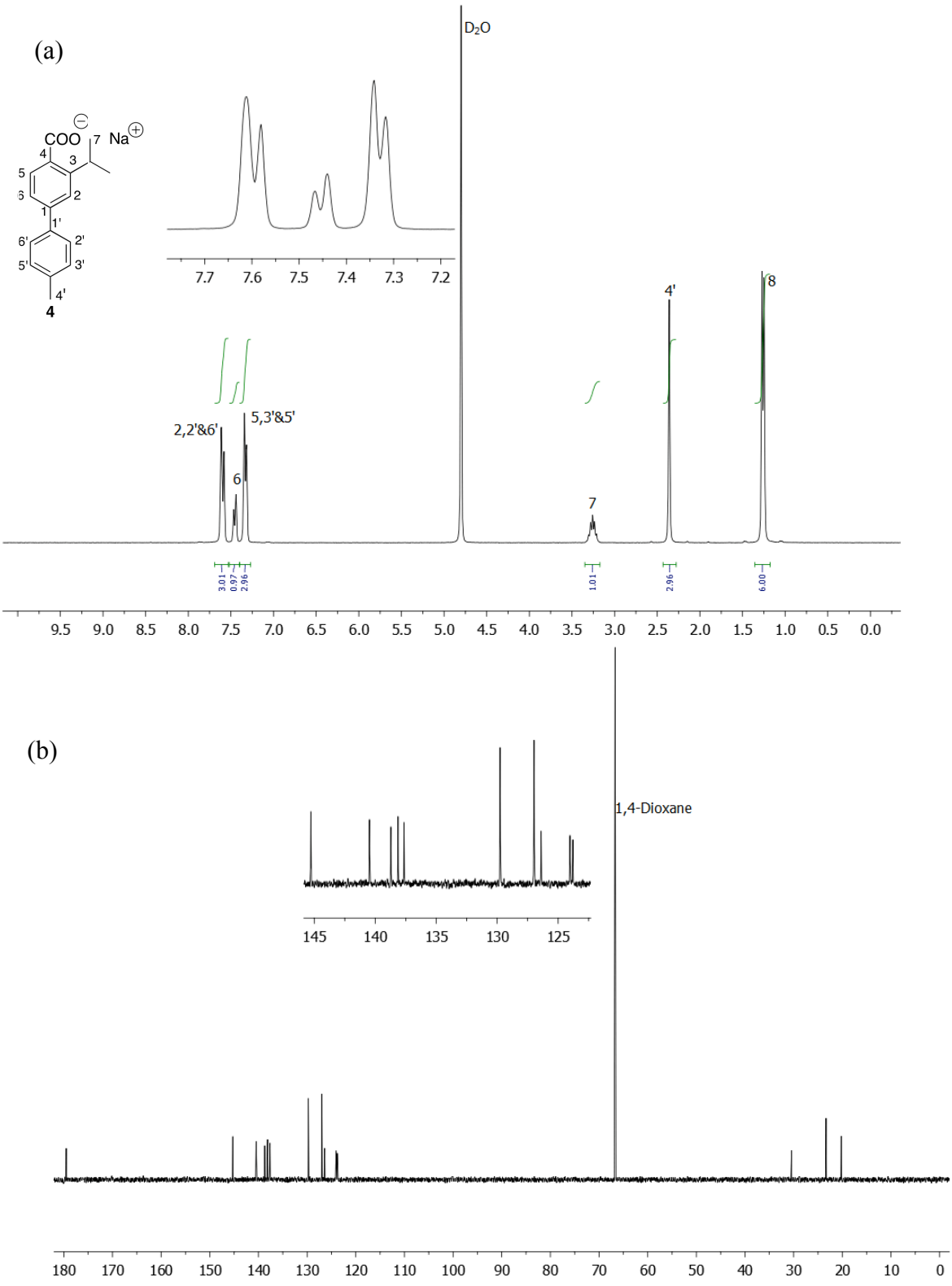


**Figure 4.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of sulfonium salt **4** in $D_2O$ (reference used for $^{13}$C NMR is 1,4-dioxane, δ 67.2 ppm).

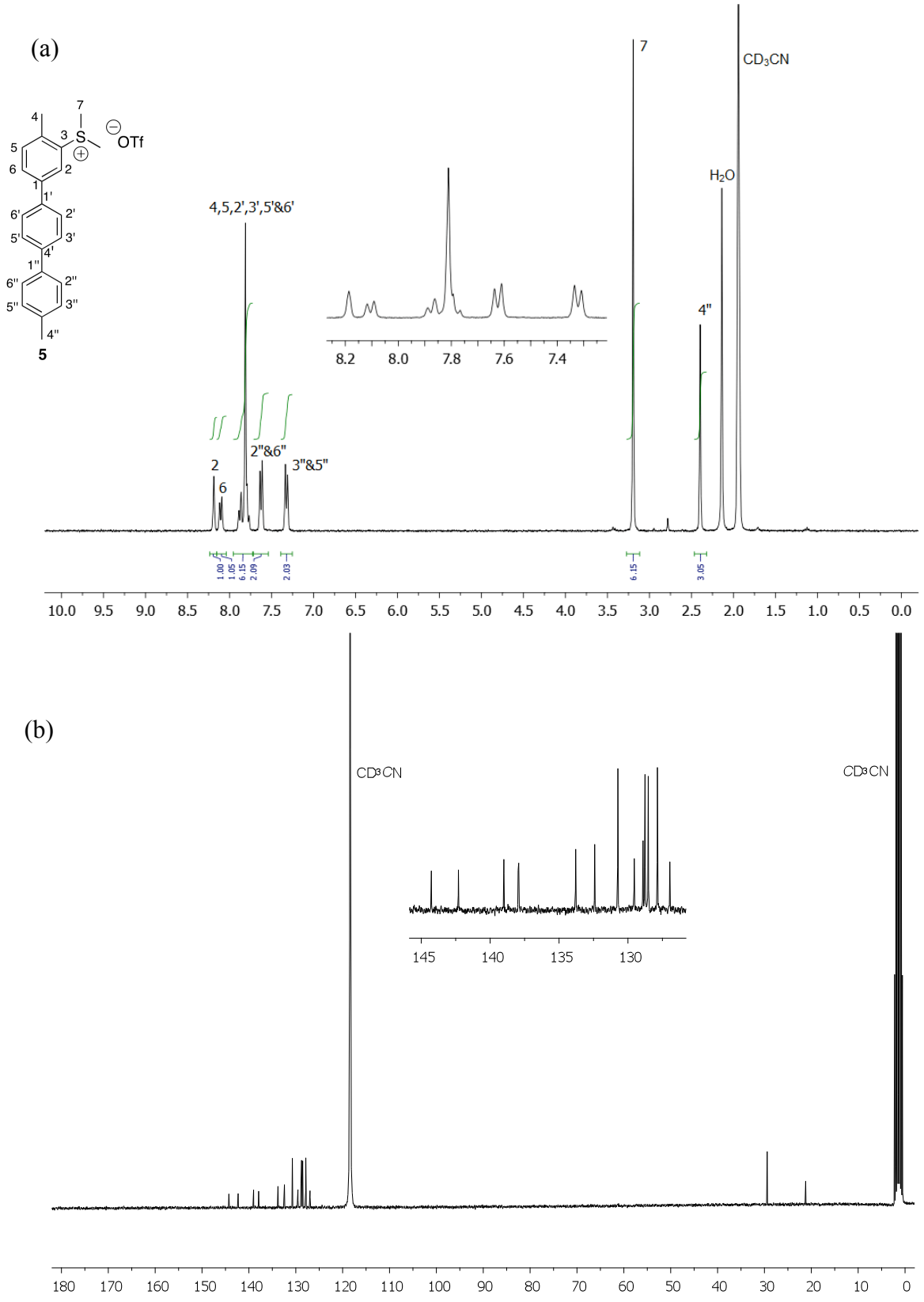


**Figure 5.** (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of terphenyl **5** in $CD_3CN$.

## 2. $^1$H NMR characterization of assemblies 1•CB[7] – 4•CB[7]

**1•CB[7]**. Cucurbit[7]uril (1.6 mg) was added to a solution of biphenyl **1** (2.0 mM) in $D_2O$ (0.70 mL). $^1$H NMR ($D_2O$): δ 8.26 (s, Ar-*H*, 1H), 8.09 (br, Ar-C*H*$_3$, 1H), 7.75 (m, Ar-*H*, 2H), 6.87 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 6.43 (d, *J* = 7.8 Hz, Ar-*H*, 2H), 5.75 (d, *J* = 15.0 Hz, CB[7], 14H), 5.46 (s, CB[7], 14H), 4.16 (d, *J* = 15.0 Hz, CB[7], 14H), 3.48 (s, S(C*H*$_3$)$_2$, 6H), 1.91 (s, Ar-C*H*$_3$, 3H) ppm.

**2•CB[7]**. Prepared similarly with biphenyl **2**. $^1$H NMR ($D_2O$): δ 8.22 (d, *J* = 5.4 Hz, Ar-*H*, 1H), 8.05 (t, *J* = 6.6 Hz, Ar-*H*, 1H), 7.50 (t, *J* = 10.2 Hz, Ar-*H*, 1H), 6.81 (d, *J* = 7.8 Hz, Ar-*H*, 2H), 6.42 (d, *J* = 7.5 Hz, Ar-*H*, 2H), 5.75 (br, CB[7], 14H), 5.45 (s, CB[7], 14H), 4.18 (d, *J* = 15.3 Hz, CB[7], 14H), 3.56 (s, S(C*H*$_3$)$_2$, 6H), 1.91 (s, Ar-C*H*$_3$, 3H) ppm.

**3•CB[7]**. Prepared similarly with biphenyl **3**. $^1$H NMR ($D_2O$): δ 8.35 (s, Ar-*H*, 1H), 8.07 (d, *J* = 8.1 Hz, Ar-*H*, 1H), 7.58 (d, *J* = 8.1 Hz, Ar-*H*, 1H), 6.92 (d, *J* = 8.1 Hz, Ar-*H*, 2H), 6.39 (d, *J* = 7.5 Hz, Ar-*H*, 2H), 5.78 (br, CB[7], 14H), 5.49 (s, CB[7], 14H), 4.20 (d, *J* = 15.0 Hz, CB[7], 14H), 3.57 (s, S(*CH*$_3$)$_2$, 6H), 2.70 (s, Ar-C*H*$_3$, 3H), 1.87 (s, Ar-C*H*$_3$, 9H) ppm.

**4•CB[7]**. Prepared similarly with biphenyl **4**. $^1$H NMR ($D_2O$): δ 7.90 (br, Ar-*H*, 1H), 7.66 (br, Ar-*H*, 1H), 7.35 (d, *J* = 3.9 Hz, Ar-*H*, 1H), 7.19 (br, Ar-*H*, 2H), 6.55 (br, Ar-*H*, 2H), 5.78 (d, *J* = 9.0 Hz, CB[7], 49H), 5.52 (s, CB[7], 49H), 4.22 (d, *J* = 9.3 Hz, CB[7], 49H), 3.29 (br, Ar-C*H*, 1H), 1.88 (br, Ar-C*H*$_3$, 3H), 1.43 (br, CH(C*H*$_3$)$_2$, 6H) ppm.

## 3. Titration of biphenyls 1 – 4 with increasing amounts of CB[7]

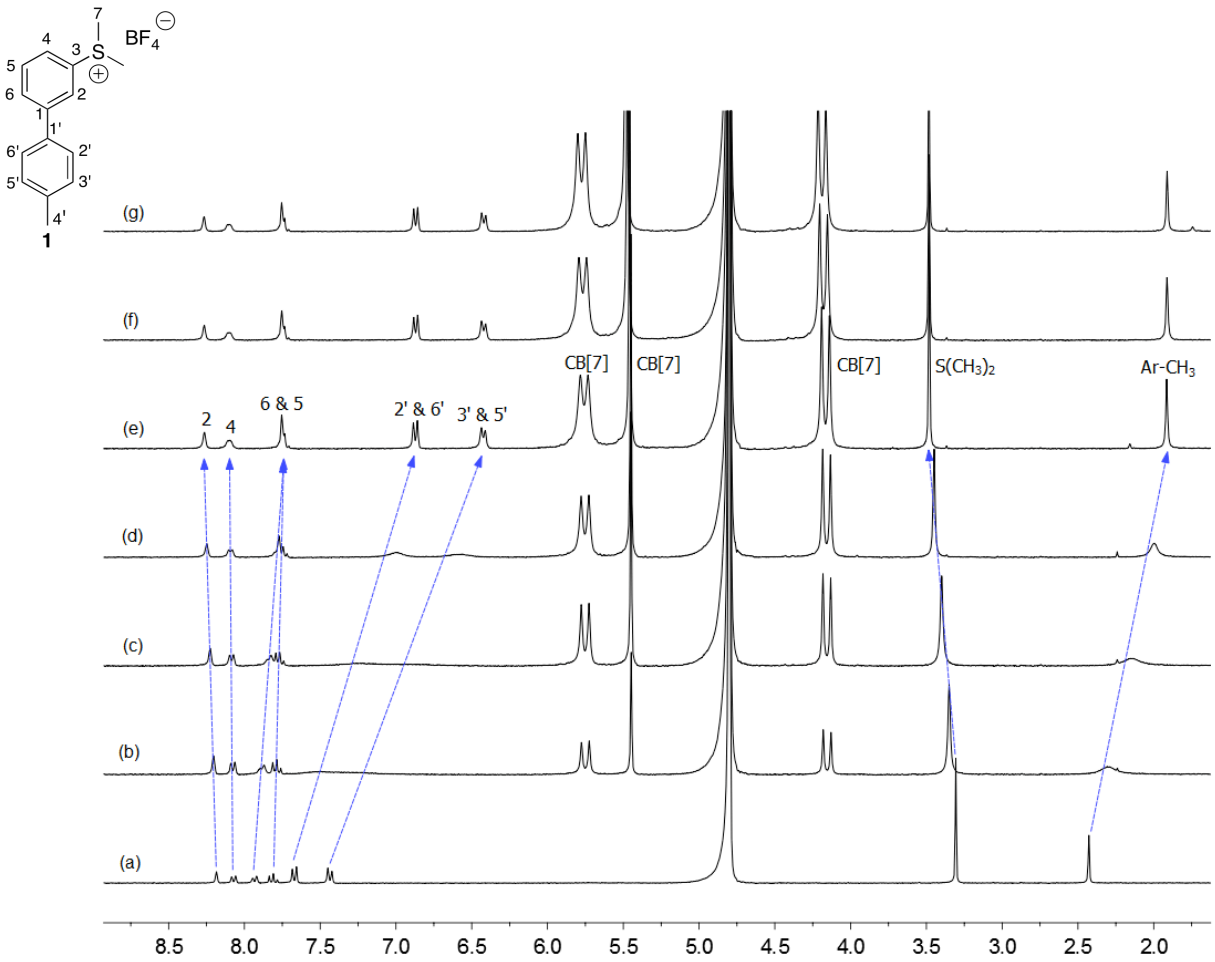


**Figure 6.** $^{1}$H NMR spectra of biphenyl **1** (2.0 mM) in $D_2O$ (0.70 mL) (a) in the absence of CB[7], and (b) – (g) with increasing amounts of CB[7] (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM).

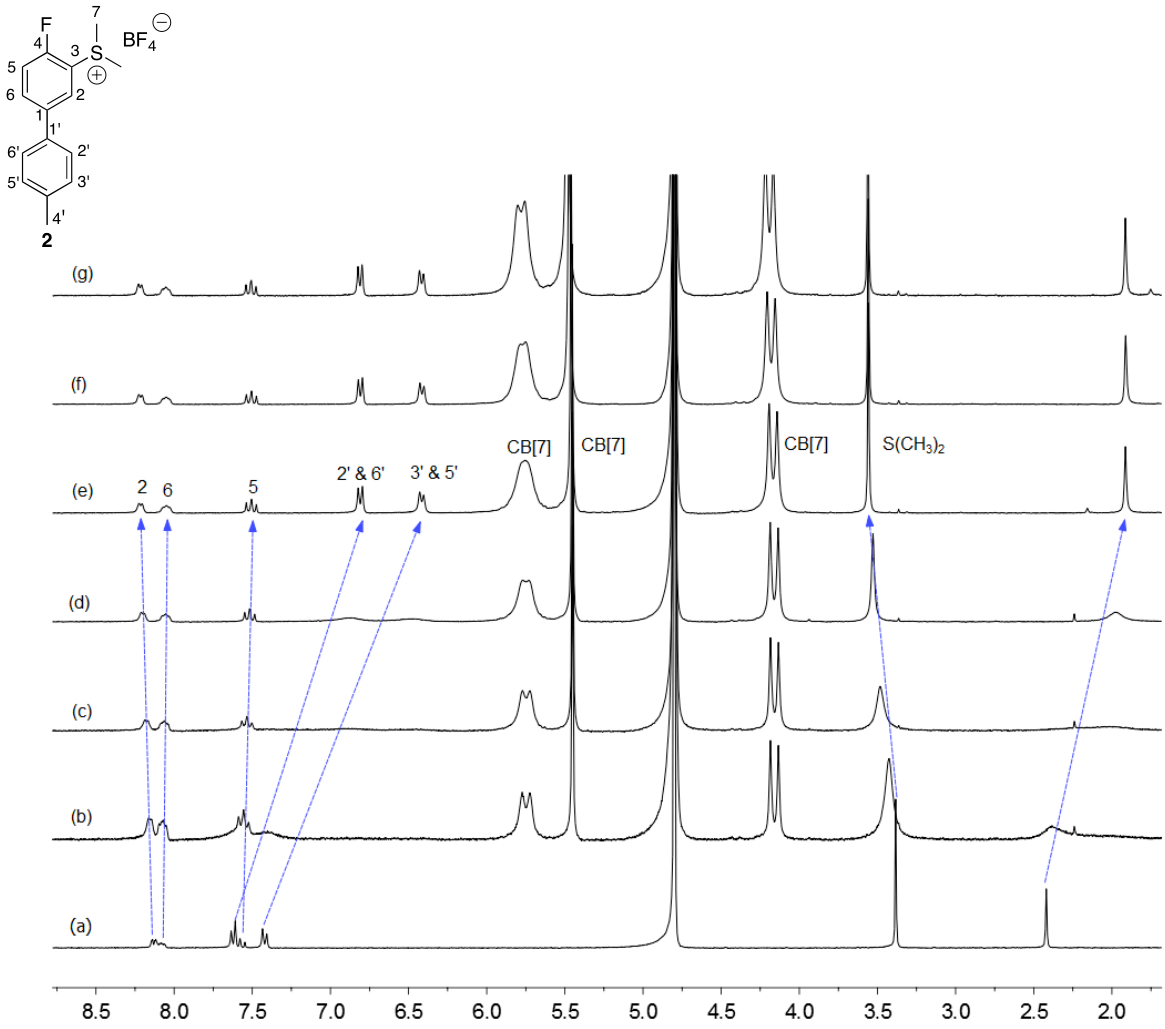


**Figure 7.** $^{1}$H NMR spectra of biphenyl **2** (2.0 mM) in $D_2O$ (0.70 mL) (a) in the absence of CB[7], and (b) – (g) with increasing amounts of CB[7] (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM).

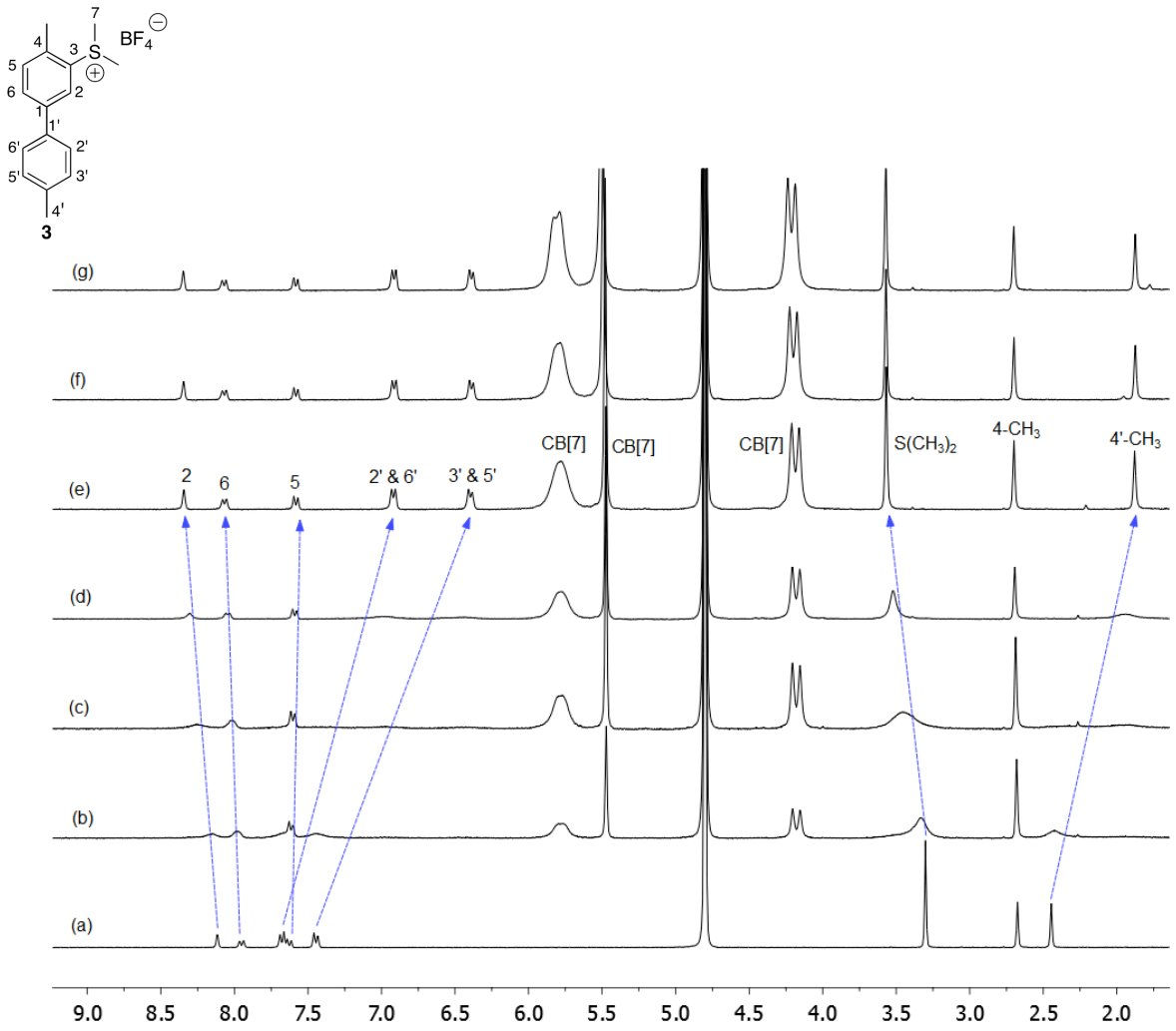


**Figure 8.** $^{1}$H NMR spectra of biphenyl **3** (2.0 mM) in $D_2O$ (0.70 mL) (a) in the absence of CB[7], and (b) – (g) with increasing amounts of CB[7] (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM).

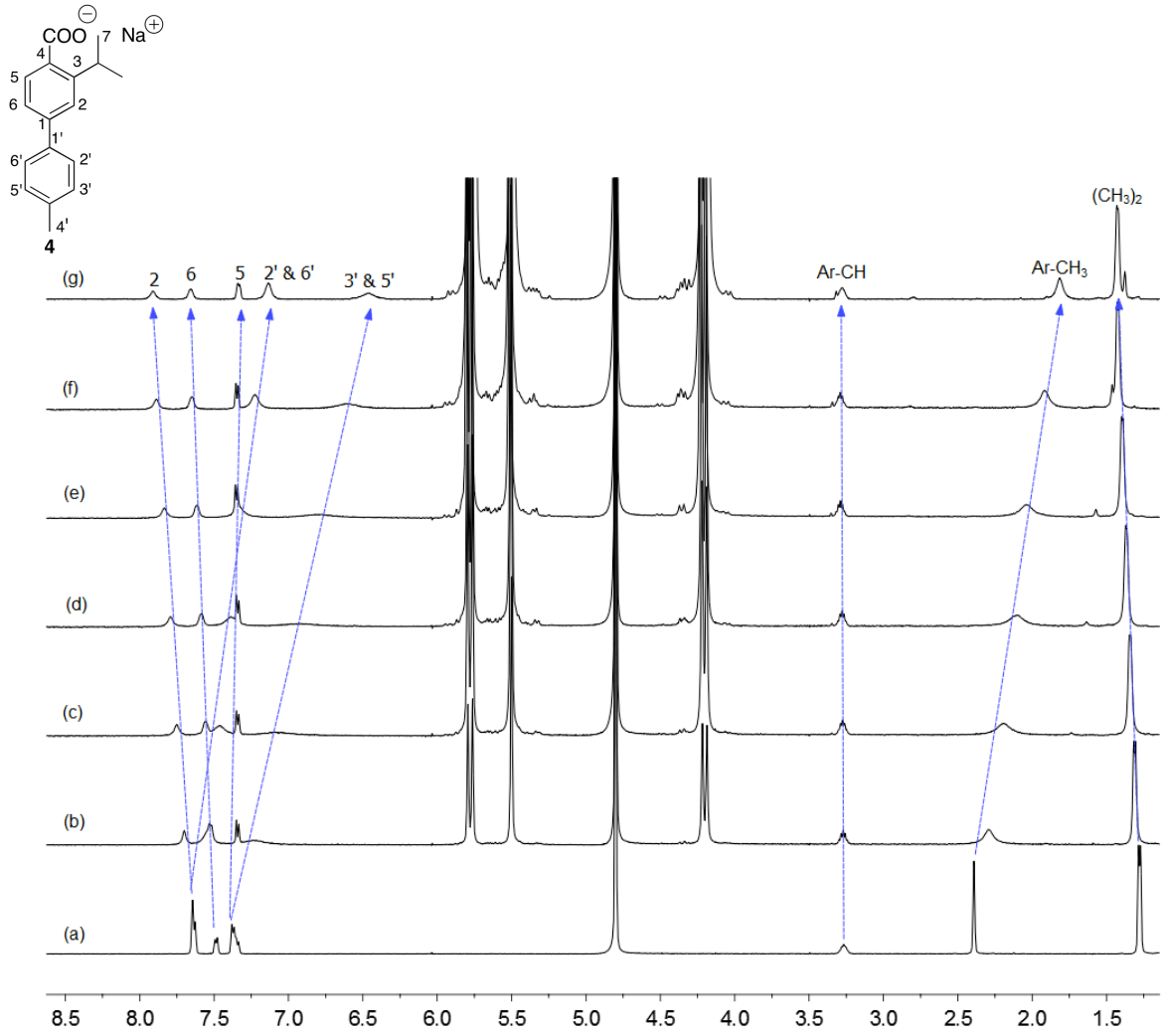


**Figure 9.** $^{1}$H NMR spectra of biphenyl **4** (2.0 mM) in $D_2O$ (0.70 mL) (a) in the absence of CB[7], and (b) – (g) with increasing amounts of CB[7] (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mM).

## 4. ITC experiments on the complexation of CB[7] with guests 1 – 5

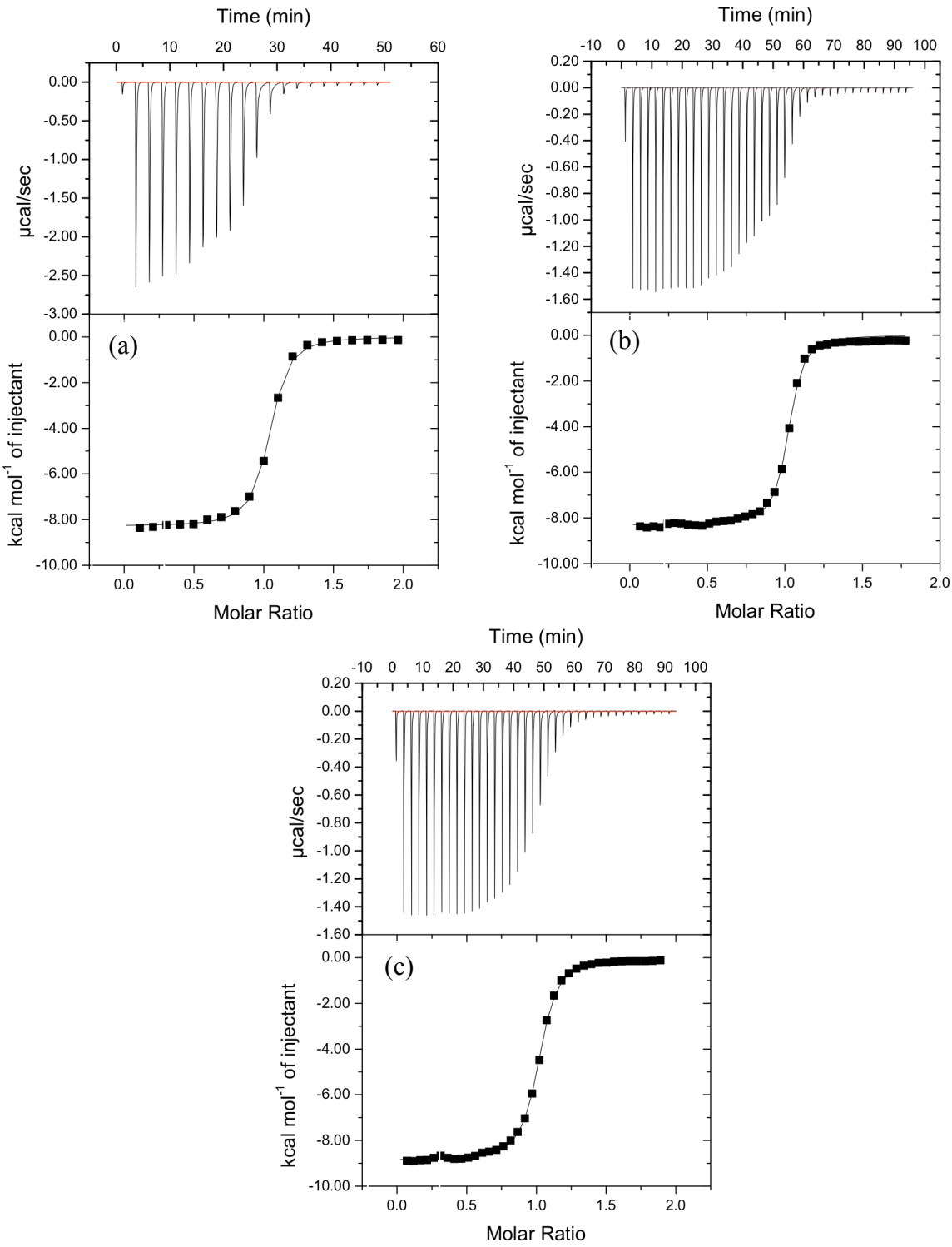


**Figure 10.** ITC experiment on complexation of (a) biphenyl **1** (2.0 mM), (b) biphenyl **2** (2.0 mM) and (c) biphenyl **3** (2.0 mM) with CB[7] (0.22 mM) in water at 25 °C.

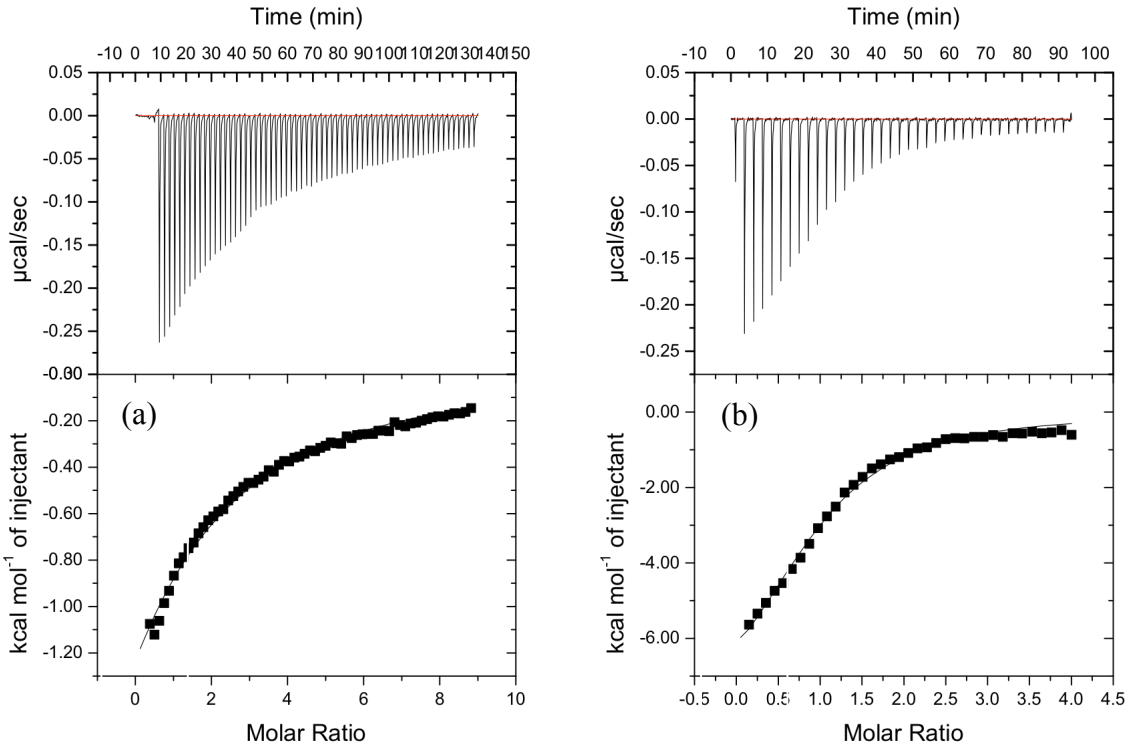


**Figure 11.** ITC experiments on complexation of (a) biphenyl **4** (10 mM) and (b) terphenyl **5** (0.50 mM) with CB[7] (0.23 mM and 24 µM, respectively) in water at 25 °C.