The Role of Attractive van der Waals Forces in the Catalysis of Michael Addition by a Phenyl Decorated Uranyl Salophen Complex.

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Supporting Information

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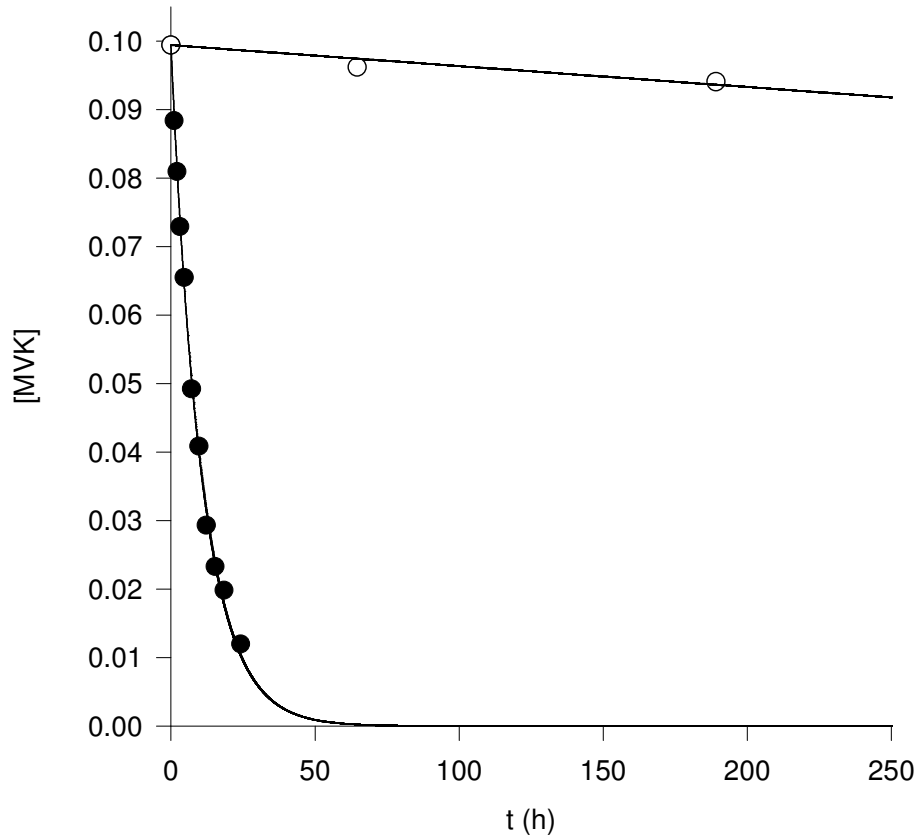

Figure 1S. Time-concentration profiles for Michael addition of 2-carboethohy-cyclopentanone to MVK in $CDCl_3$, at 25 °C. [MVK] = 0.10 M, [2-carboethohy-cyclopentanone] = 0.20 M, and $[Et_3N] = 5.0 \cdot 10^{-3}$ M. (●) [**2b**] = $2.0 \cdot 10^{-3}$ M; (○) no metal catalyst. The points are experimental and the curves are drawn for clarity purposes only.

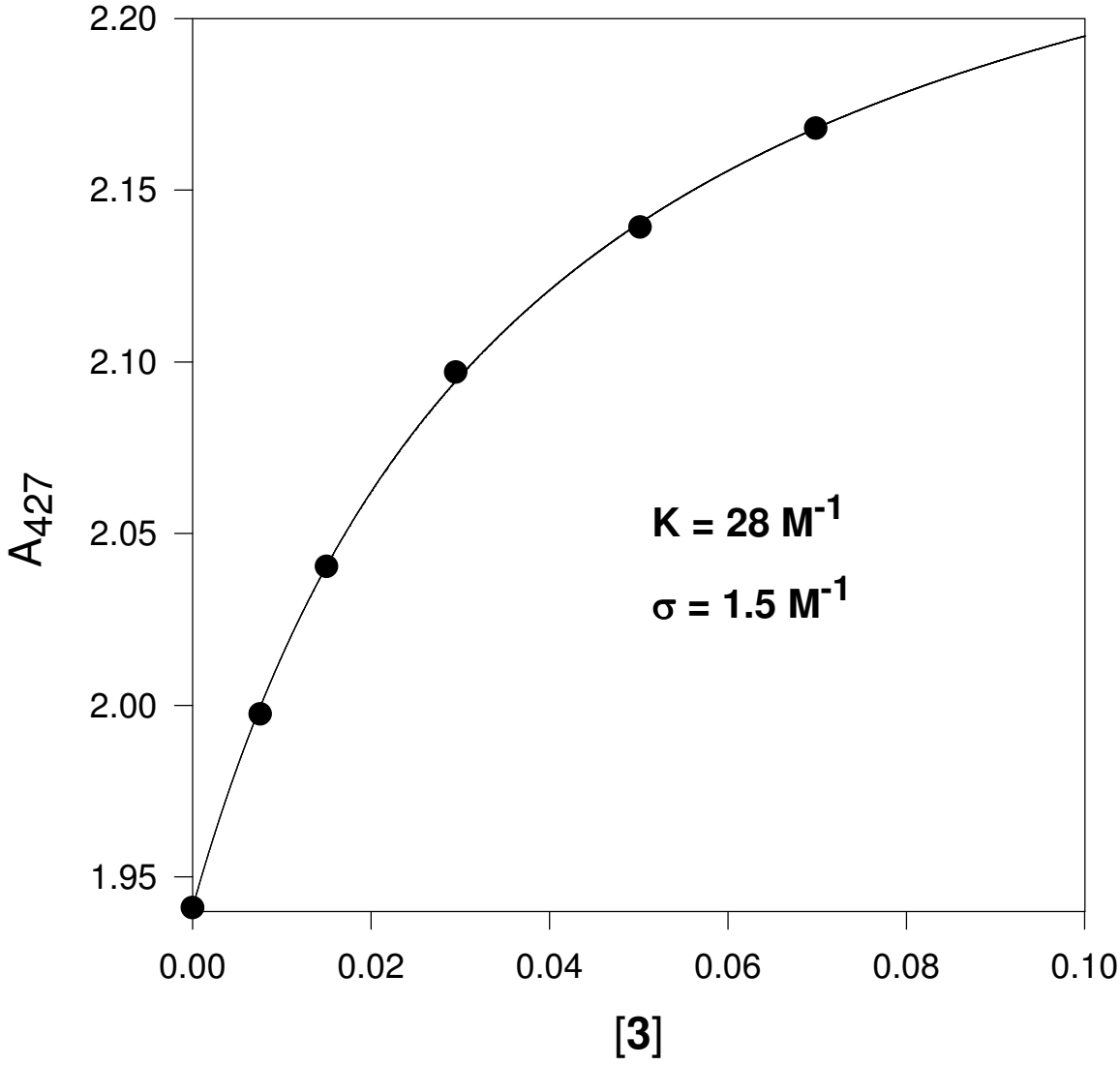

Figure 2S. Spectrophotometric titration of compound **2b** with compound **3**.

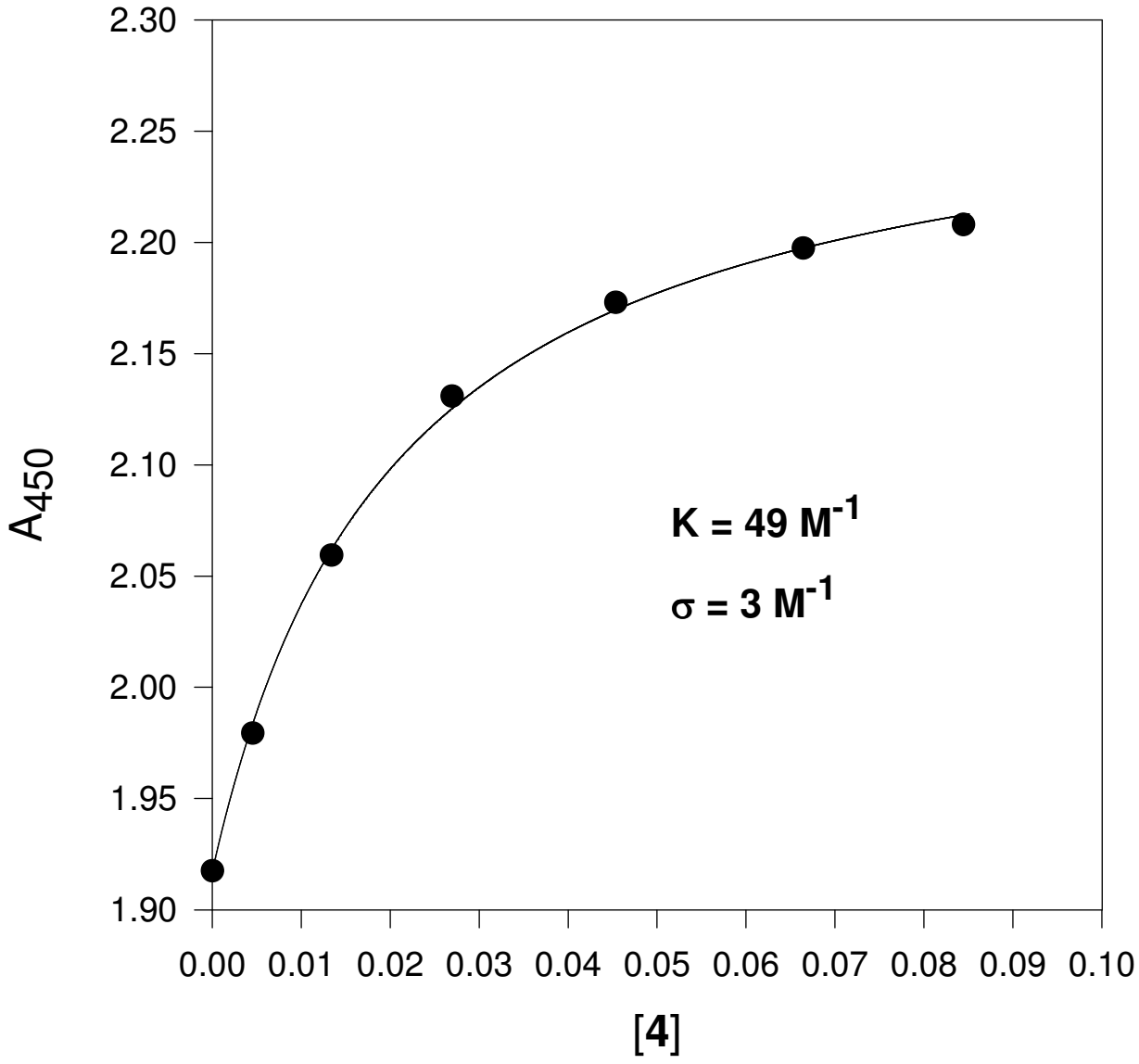

Figure 3S. Spectrophotometric titration of compound **2b** with compound **4**.

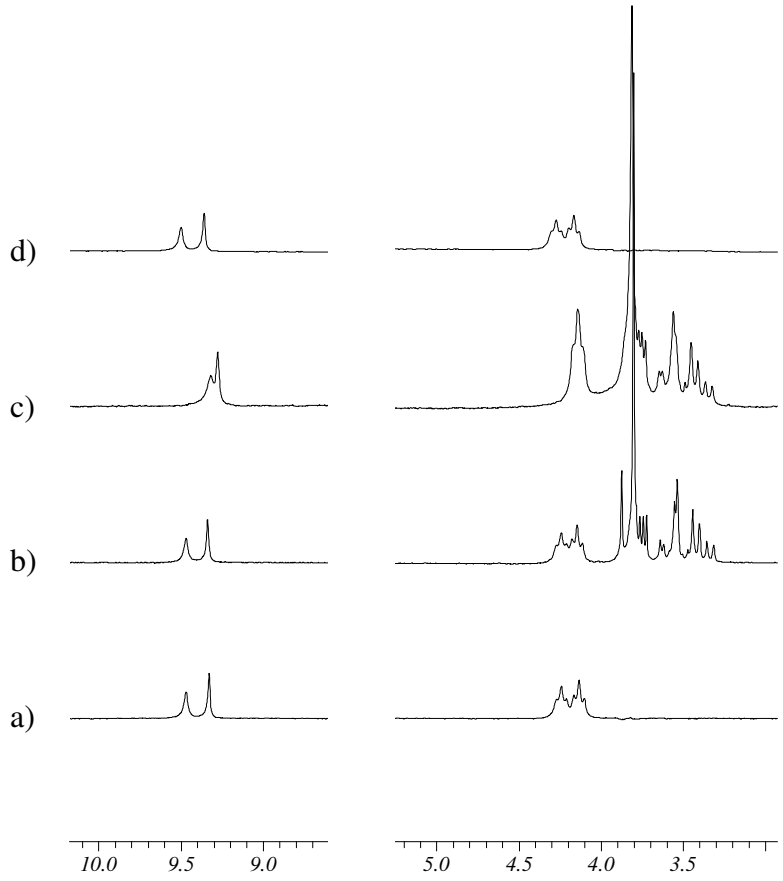

Figure 4S. Portions of ^{1}H NMR spectral regions of $CDCl_3$ solutions of a) compound **2b**; b) **2b** and **3**; c) **2b**, **3**, and Et_3N; d) **2b** and Et_3N. Concentration of **2b** is always 5 mM; concentrations of **3** and Et_3N are always 10 mM. The signals at 9.5 - 9.3 p.p.m. correspond to the resonances of protons on the imine carbon of **2b**, -C(H)=N-; the signals at 4.4 – 4.1 p.p.m. correspond to the resonances of protons of the first methylene groups of the alkoxy chains of **2b**, -O-C$(H)_2$-. It is clearly seen that no changes are produced on the spectrum of **2b** nor upon addition of methyl 1-oxoindane-2-carboxylate **3**, neither upon addition of Et_3N. Evident changes are instead observed when both the β-ketoester **3** and Et_3N are simultaneously present, suggesting that a complex is formed between uranyl-salophen catalyst **2b** and the enolate of **3**.

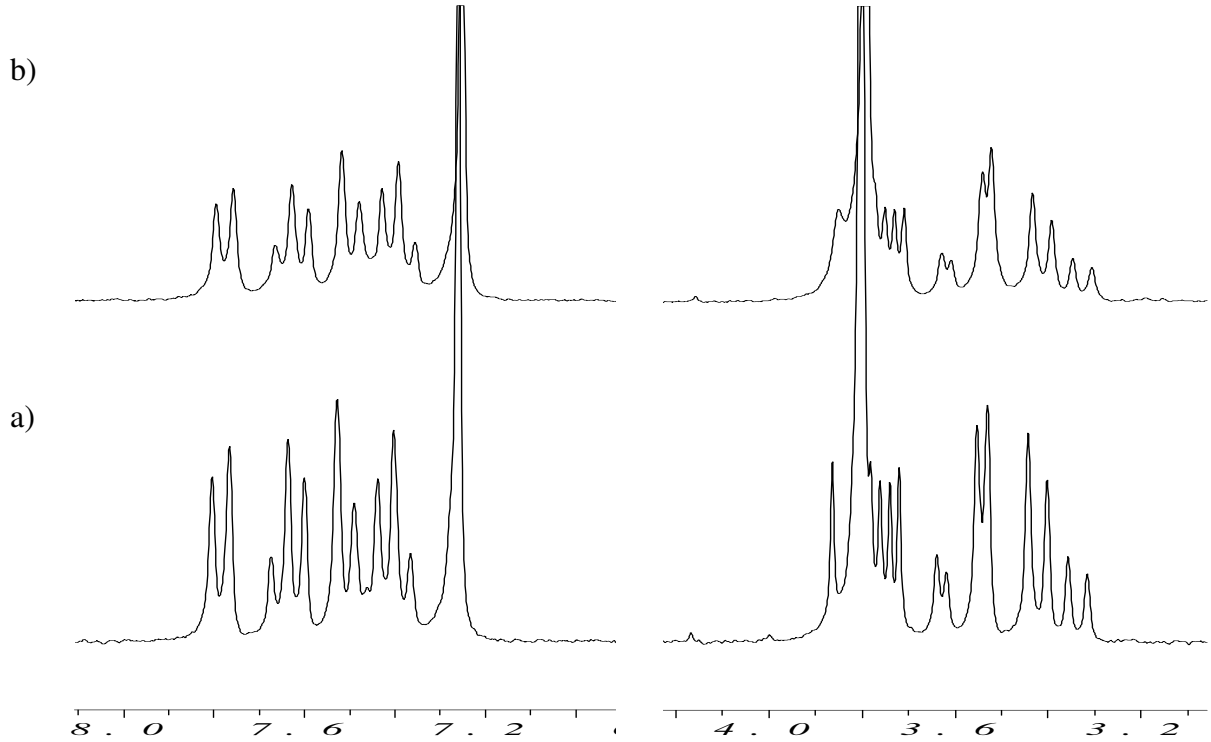

Figure 5S. Portions of ^{1}H NMR spectral regions of $CDCl_3$ solutions of a) 0.011 M compound **3**; b) 0.010 M compound **3** and 0.010 M Et_3N. The two double doublets at 3.7 – 3.3 p.p.m. correspond to the resonances of the protons of the methylene group of methyl 1-oxoindane-2-carboxylate **3**, Ar-$C(H)_2$-CH. Line broadening in spectrum (b) is due to faster racemisation of the neighbouring chiral carbon atom in the presence of the tertiary base. It is apparent that the β-ketoester is not deprotonated by Et_3N, indicating that spectral changes in the spectrum (c) of Figure 4S are due to the increased acidity of **3** upon complexation with the uranyl-salophen compound **2b**.

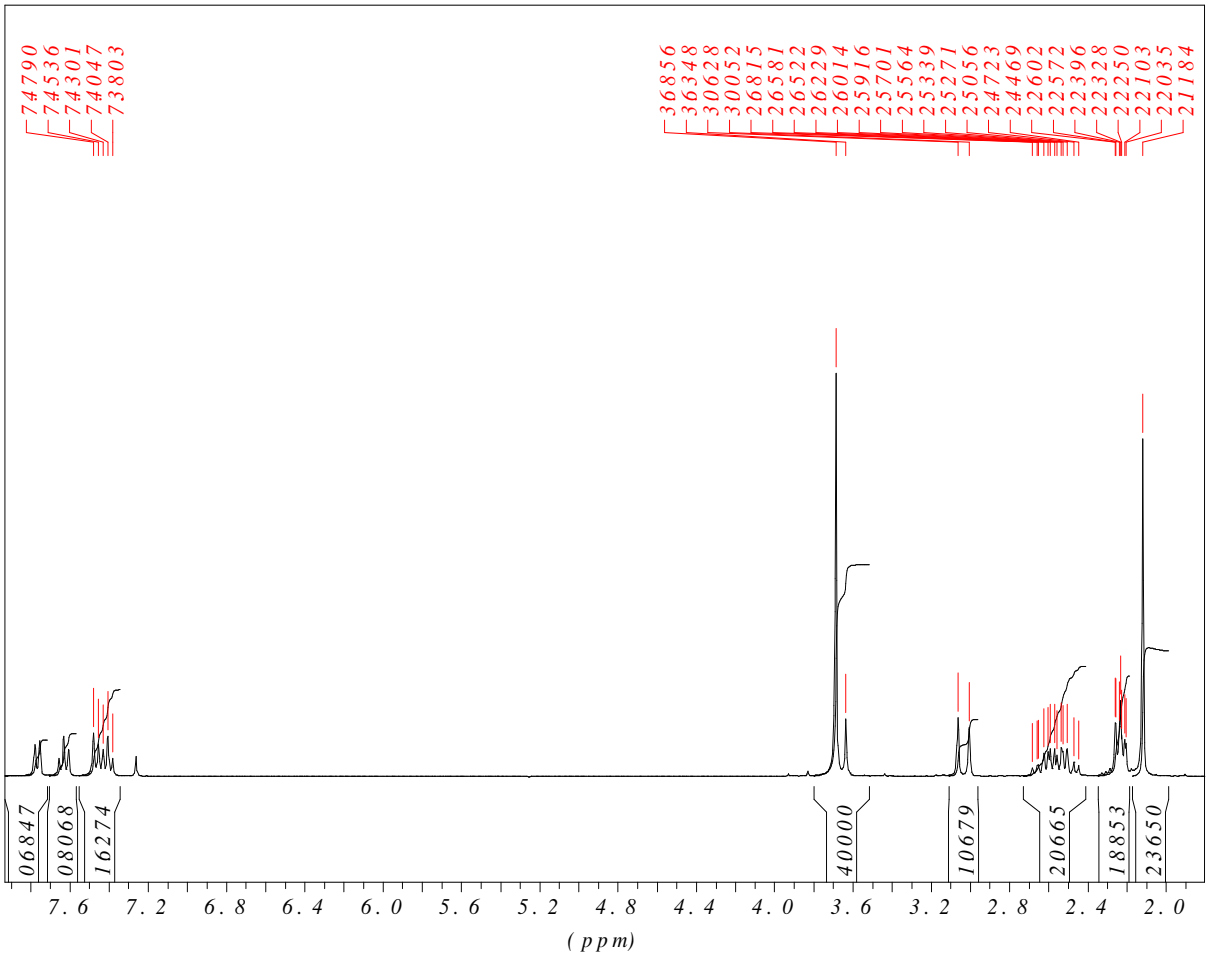

Figure 6S. ^{1}H NMR spectrum of compound **4** at 200 MHz in $CDCl_3$). δ (p.p.m): 7.76 (d, 1H), 7.63 (t, 1H), 7.48-7.38 (m, 2H), 3.69-3.63 (m, 4H), 3.03 (d, 1H), 2.68-2.45 (m, 2H), 2.26-2.20 (m, 2H), 2.12 (s, 3H).