Supporting Information

An Evaluation of Substituent Effects on Aromatic Edge-to-Face Interactions and CF-π Versus CH-π Interactions Using an Imino Torsion Balance Model

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Table S1. Chemical shifts and coupling constants obtained by analysis of the CH_2-CH ABX system in $CDCl_3$.[a]

Compd.	X	δ H_A	δ H_B	δ H_X	J_{AX} / Hz	J_{BX} / Hz	J_{AB} / Hz
1	H	3.10	2.94	4.04	9.7	3.6	12.9
2-*Za*	2-F	3.05	2.99	4.03	6.4	6.8	13.1
2-*Zb*	2-F	3.06	2.92	4.01	10.1	3.5	12.8
3	3-F	3.06	2.90	4.01	10.1	3.3	12.9
4	4-OMe	3.05	2.90	4.08	9.9	3.4	12.8
5	H	3.06	3.15	3.76	10.2	3.4	13.1
6	3-Cl	3.07	3.17	3.70	10.6	3.0	13.1
7	3-OMe	3.09	3.16	3.82	10.6[b]	3.0[b]	12.7[b]
8	4-F	3.07	3.16	3.72	10.5	3.1	13.1
9	4-Cl	3.07	3.16	3.70	10.6	3.0	13.1
10	H (Y = OH)	2.99	3.08	3.73	10.1	3.6	13.3
11	H (Y = NO_2)	3.18	3.24	3.83	9.8	3.7	13.1

[a]Determined by a full second order analysis; unless otherwise indicated; *Za* and *Zb* signals were coincident except for compound **2.** [b]Approximate first order values due to broadening of some lines arising from slight unresolved chemical shift nonequivalence of the *Za* and *Zb* forms.

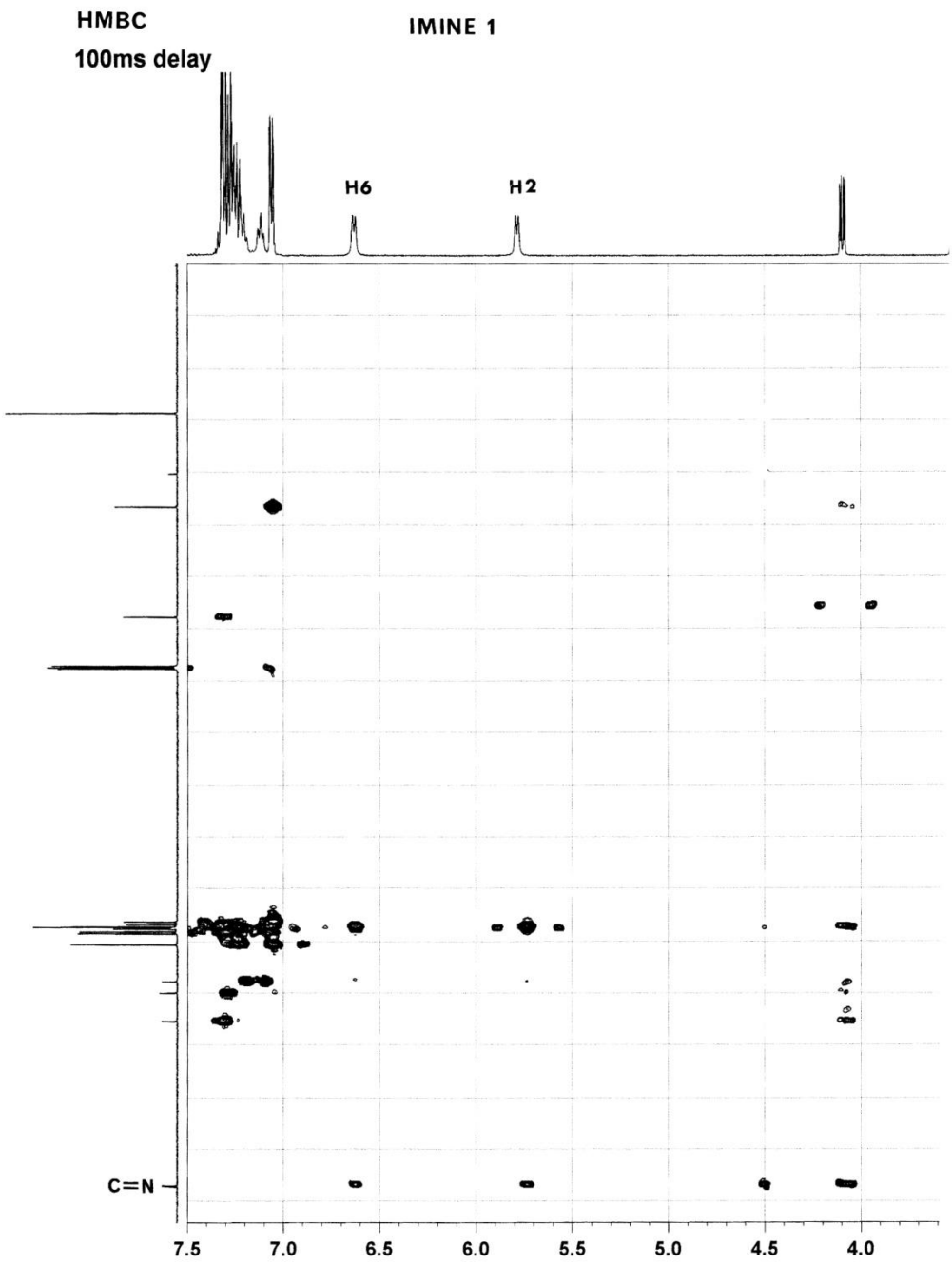


Fig. S1 2D HMBC NMR of compound **1** (500 MHz, $CDCl_3$)

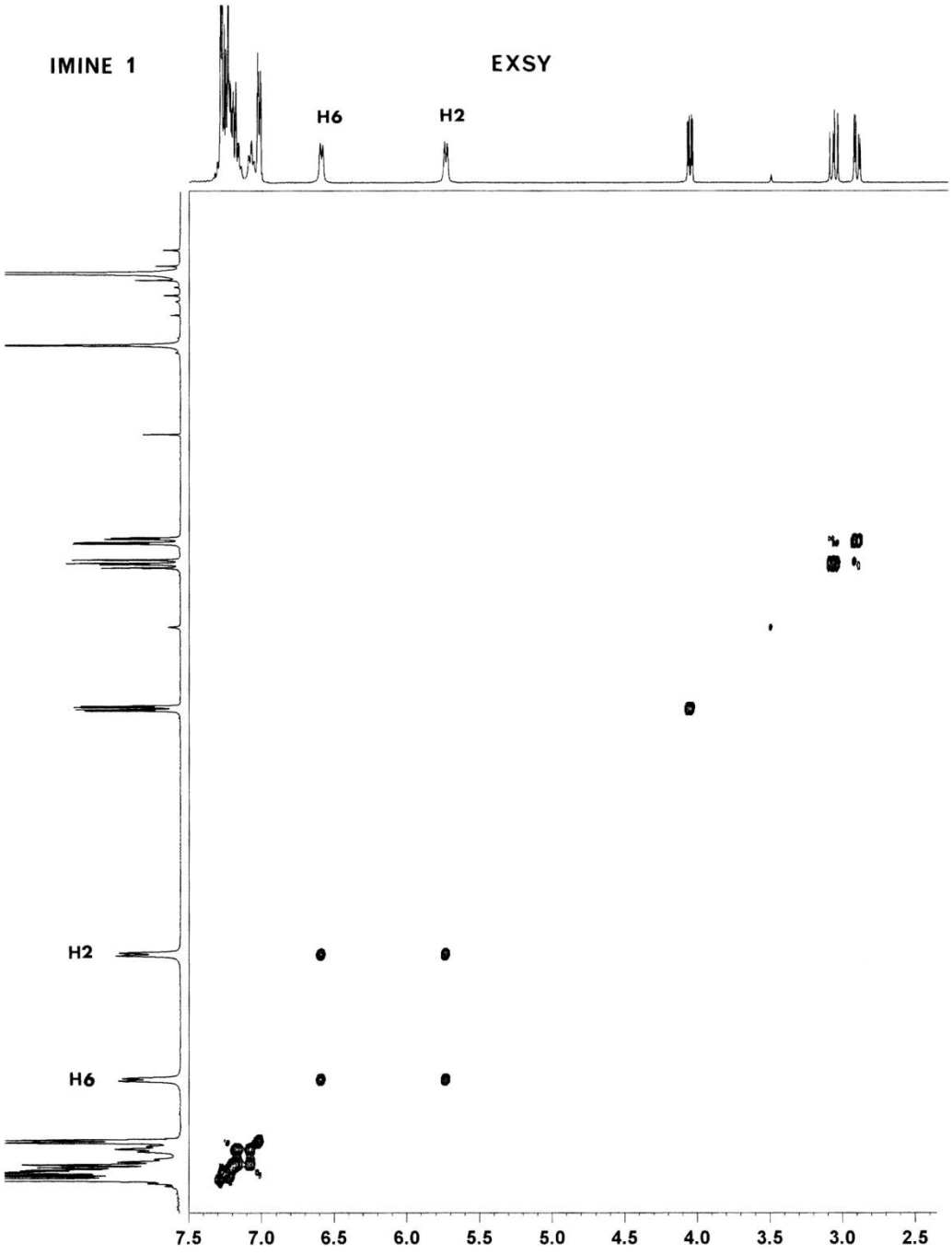


Fig. S2 2D EXSY NMR of compound **1** (500 MHz, $CDCl_3$)

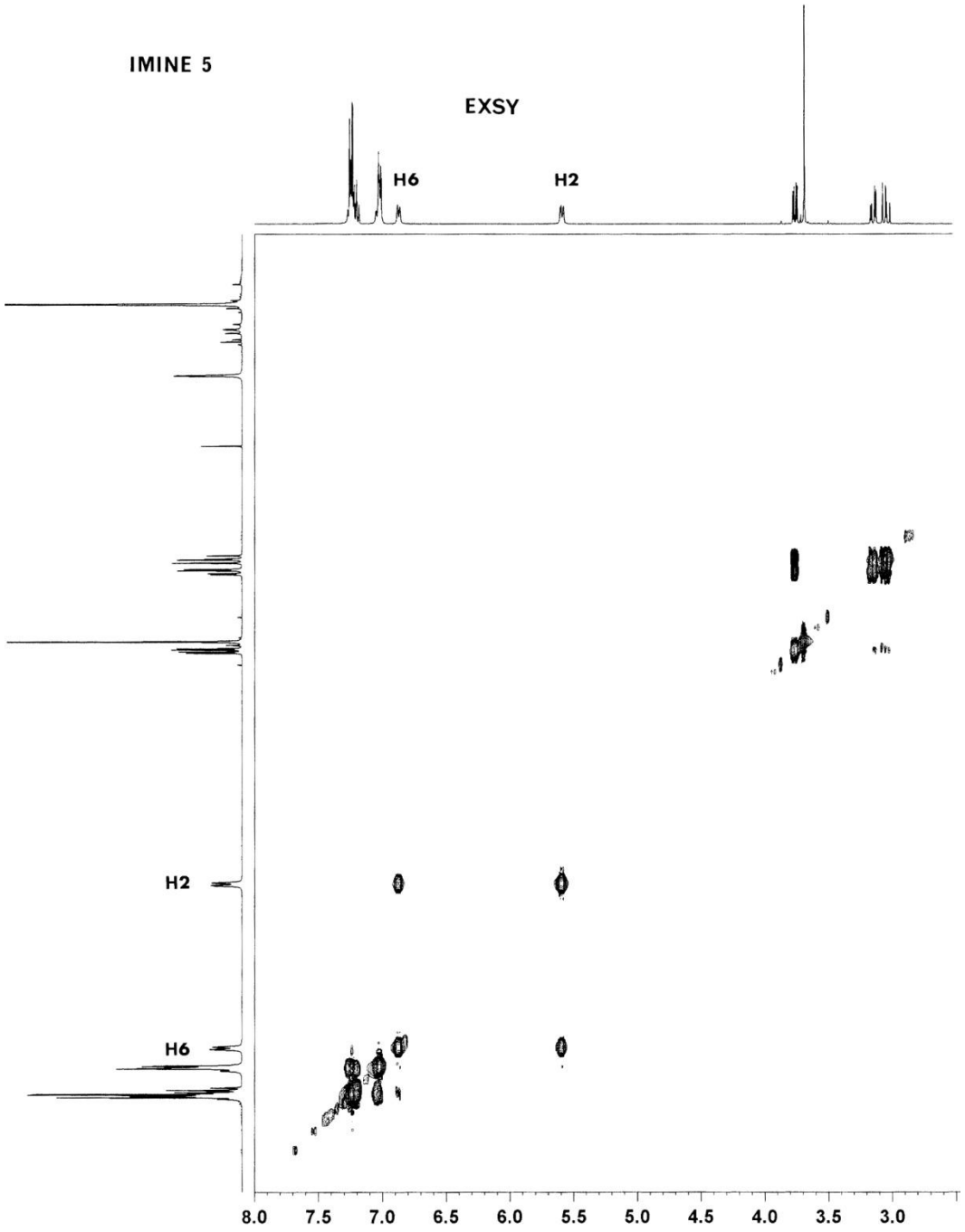
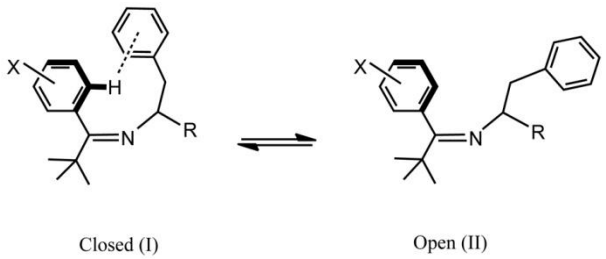


Fig. S3 2D EXSY NMR of compound **5** (400 MHz, $CDCl_3$)

Fig. S4 Methodology for modelling the rapid open-closed conformational equilibrium



Closed (I) Open (II)

Proposed open/closed rapid conformational equilibrium in compounds **1 - 11**

(i) Observed *ortho*-H chemical shift (δ_{obs}) = $P_I\delta_I + (1 - P_I)\delta_{II}$

(ii) $K_{eq} = (1\text{-}P_I)/P_I = \exp[(T\Delta S - \Delta H)/RT]$

This requires an estimate of the chemical shifts of the shielded hydrogen in the fully populated closed conformation (δ_I) and in the fully open conformation(s) (δ_{II}). Initially we thought that the open δ_{II} value should be higher than that of benzene (δ 7.3) due to the deshielding by the *ortho* imino moiety, however as the imino aryl ring in these compounds is twisted well out of the imino plane the deshielding effect may not operate. Alternatively the chemical shift of the other non-shielded *ortho*-hydrogen (δ 6.6-6.9 after correcting for substituent effects (see Table 3 in main paper) provides a somewhat different estimate. In practice a base value of δ 7.3 for δ_{II}, further adjusted for ring substituent effects, was used in the three compounds **1**, **3**, and **7** which were subjected to detailed variable temperature investigations over a wide temperature range in deuteriodichloromethane and over a shorter range in deuterio-1,1,2,2-tetrachloroethane. A value of *ca*. δ 4.7 was estimated for the closed δ_I on the basis of a predicted shielding of *ca*. 2.6 ppm obtained from Johnson–Bovey ring current shielding tables† for a hydrogen atom located 2.6 Å above the face of a benzene ring. The values of the conformational enthalpy (ΔH) and entropy (ΔS) differences were then varied in an algorithm based on the above equations to afford an optimum fit between calculated and observed shift versus temperature plots. The initial values used for δ_I and δ_{II} were adjusted for ring substituent electronic effects in the case of imines **3** and **7,** and varied over a small range to further optimise the fit to the experimental data. The model gave a good a fit to the experimental shifts over the entire temperature range as depicted in Fig.11 (main paper) for compound **1**, and for both the *Za* and *Zb* forms of compounds **3** and **7** (see ESI, pages 8-11).

† J. W. Emsley, J. Feeny and L.H. Sutcliffe, *Nuclear Magnetic Resonance Spectroscopy*, Pergamon Press, Oxford, 1965, vol. 1, pp 595-604.

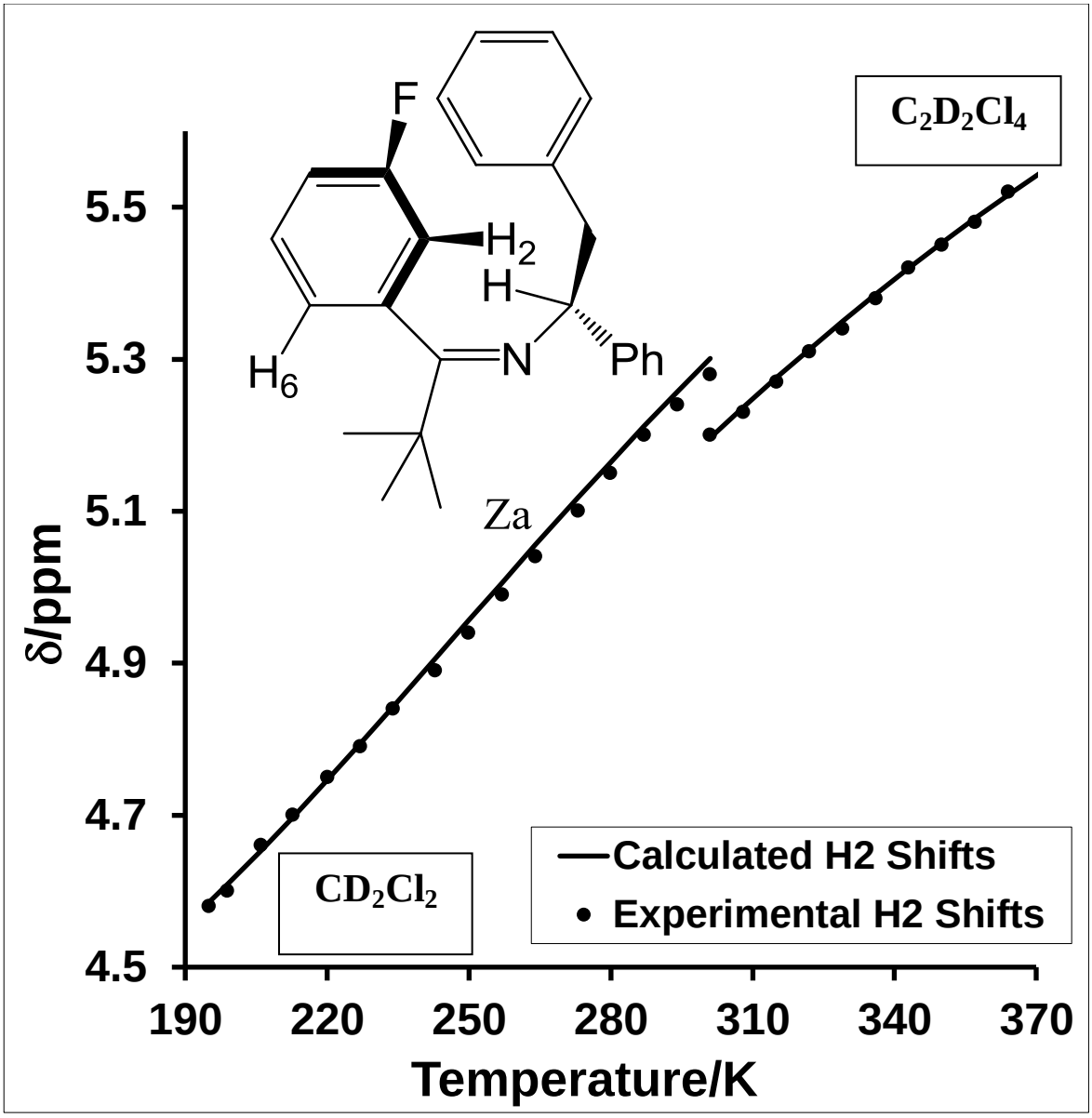


Fig. S5 Plot of observed (solid circles) and best fit calculated (lines) H2 chemical shifts versus temperature for compound **3**-*Za* in deuteriodichloromethane (lower) and deuterio-1,1,2,2-tetrachloroethane (upper).

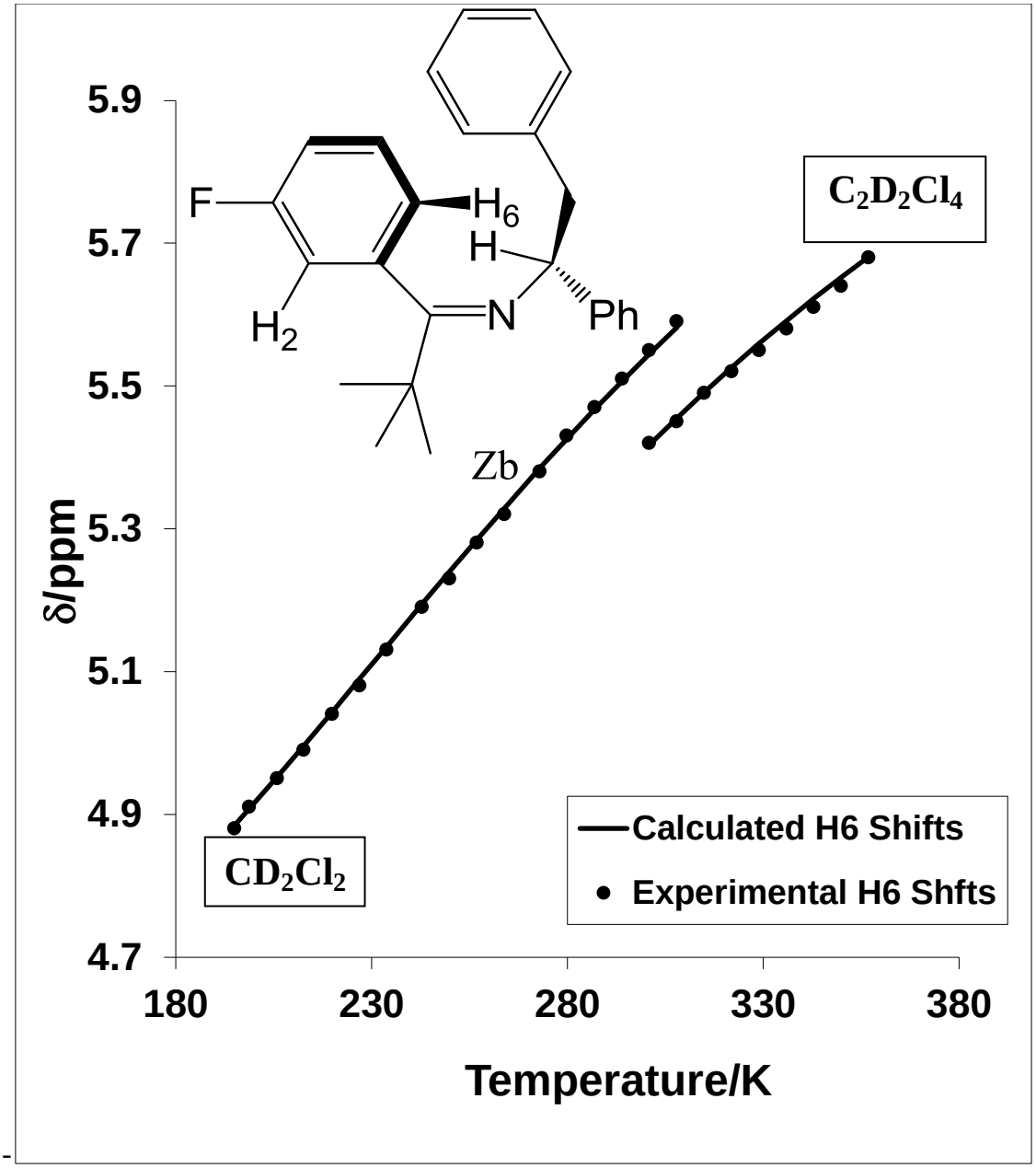


Fig. S6 Plot of observed (solid circles) and best fit calculated (lines) H6 chemical shifts versus temperature for compound **3**-*Zb* in deuteriodichloromethane (lower) and deuterio-1,1,2,2-tetrachloroethane (upper).

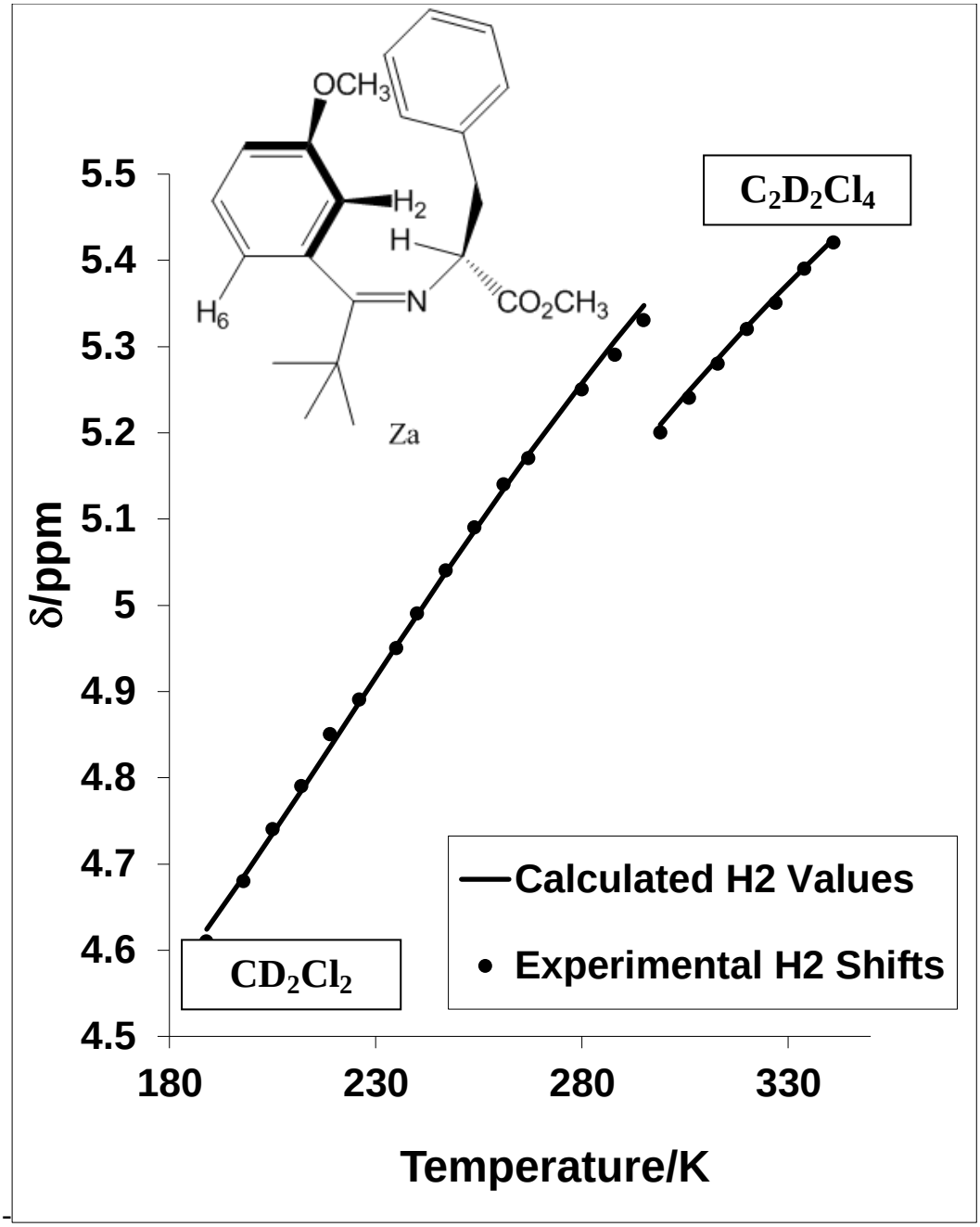


Fig. S7 Plot of observed (solid circles) and best fit calculated (lines) H2 chemical shifts versus temperature for compound **7**-*Za* in deuteriodichloromethane (lower) and deuterio-1,1,2,2-tetrachloroethane (upper).

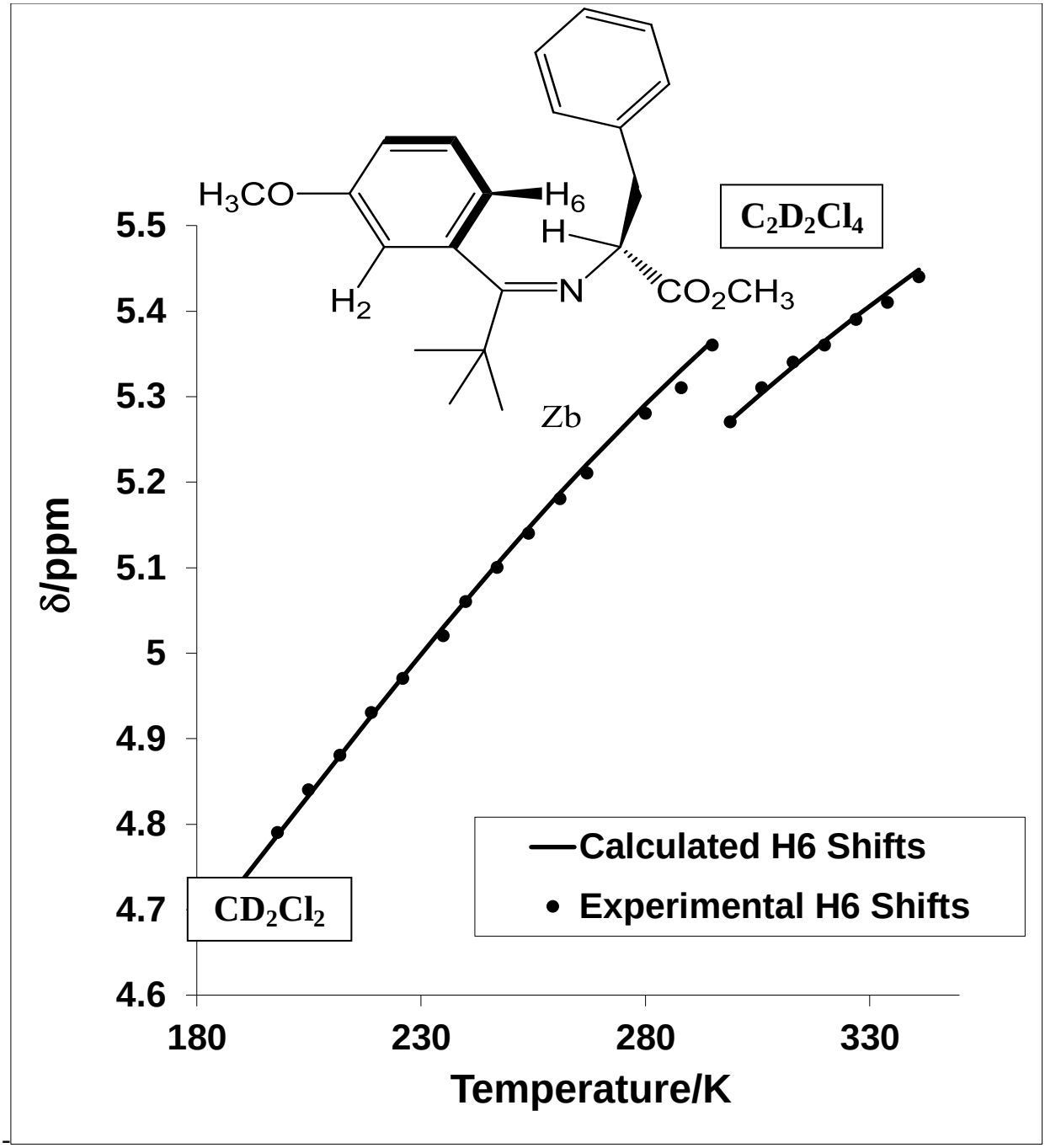


Fig. S8 Plot of observed (solid circles) and best fit calculated (lines) H6 chemical shifts versus temperature for compound **7**-*Zb* in deuteriodichloromethane (lower) and deuterio-1,1,2,2-tetrachloroethane (upper).

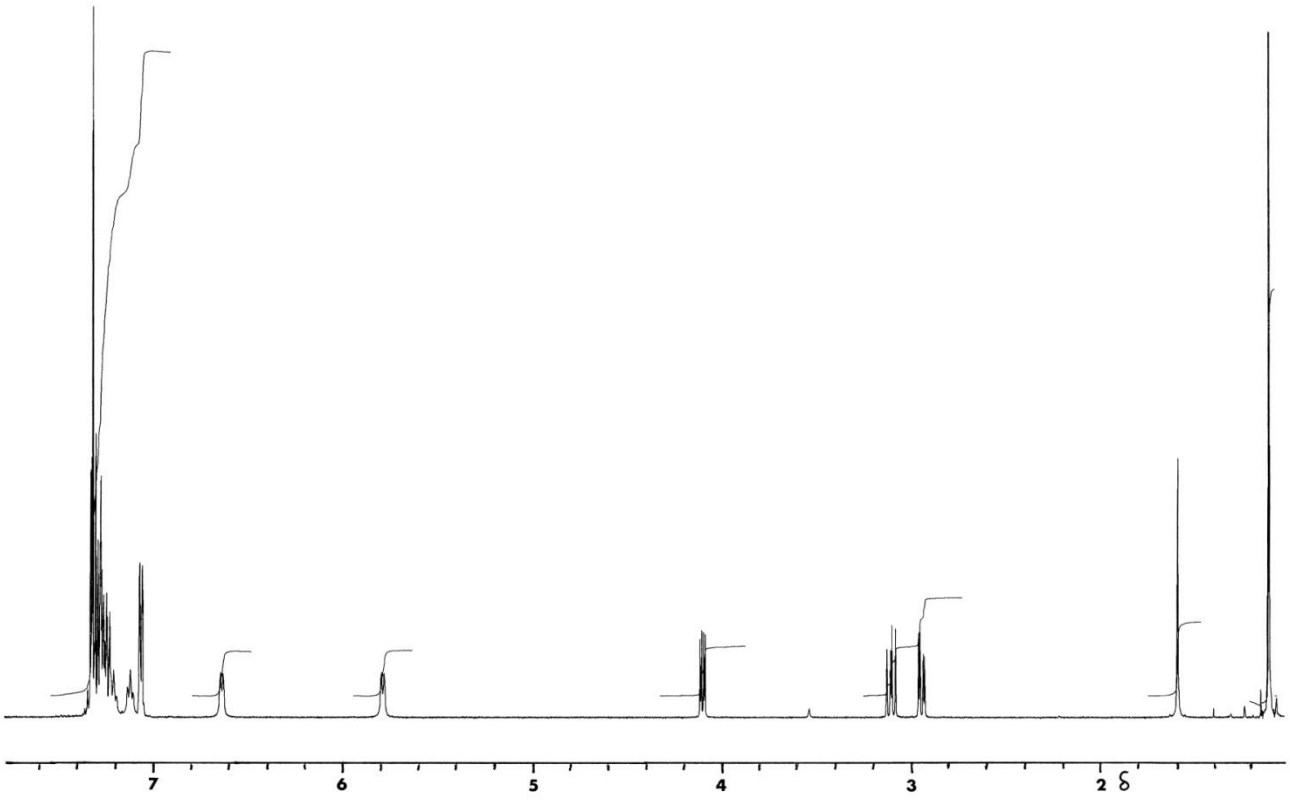


Fig. S9 ^{1}H NMR spectrum of compound **1** (500 MHz, $CDCl_3$)

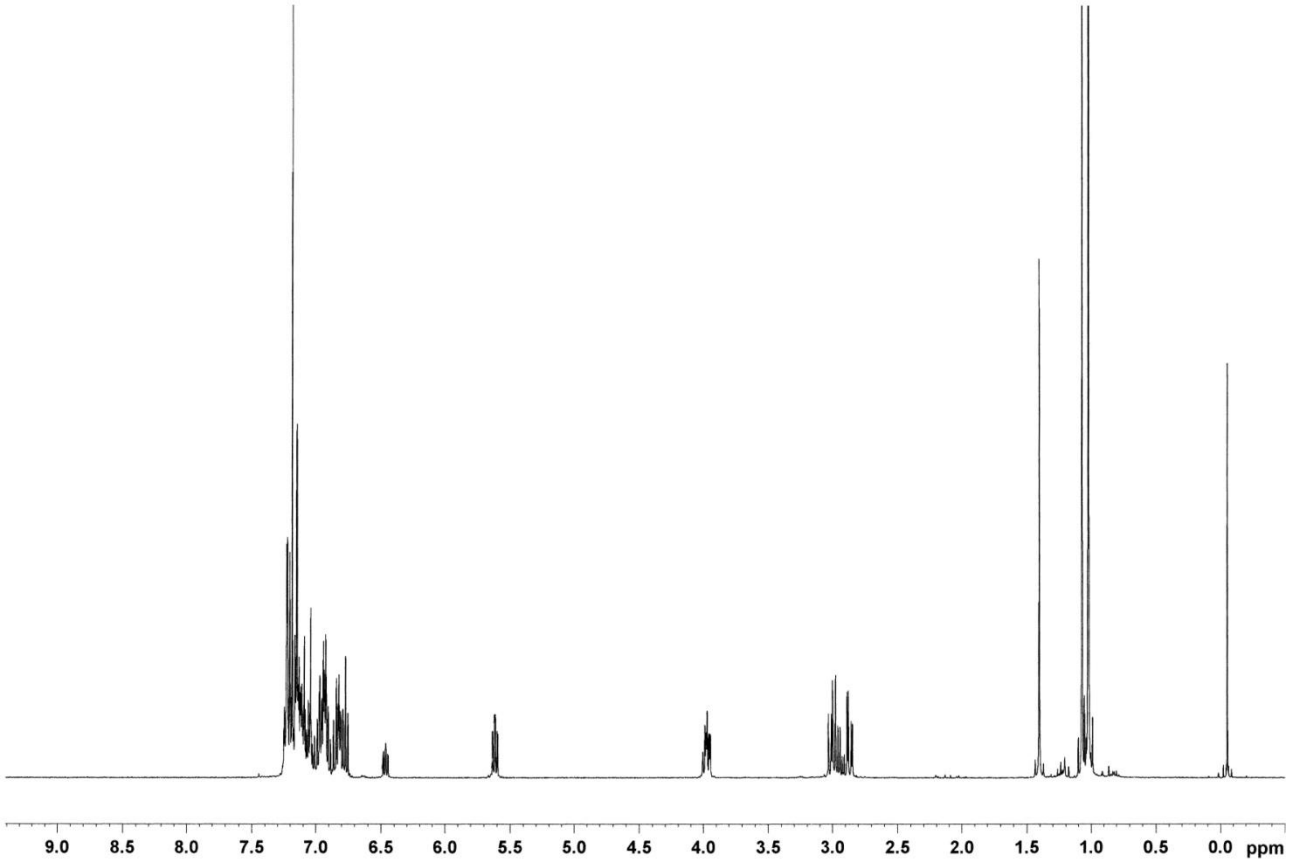


Fig. S10 ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$)

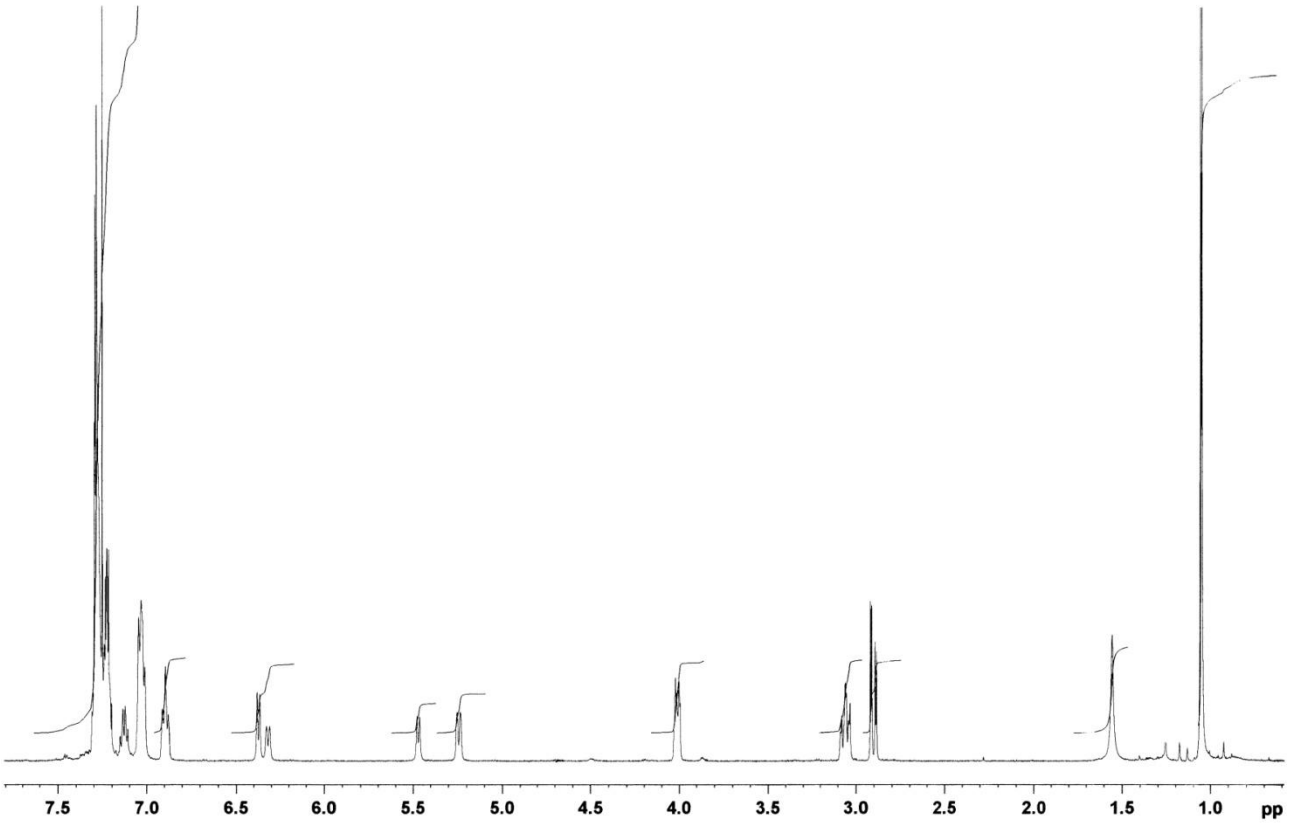


Fig. S11 ^{1}H NMR spectrum of compound **3** (500 MHz, $CDCl_3$)

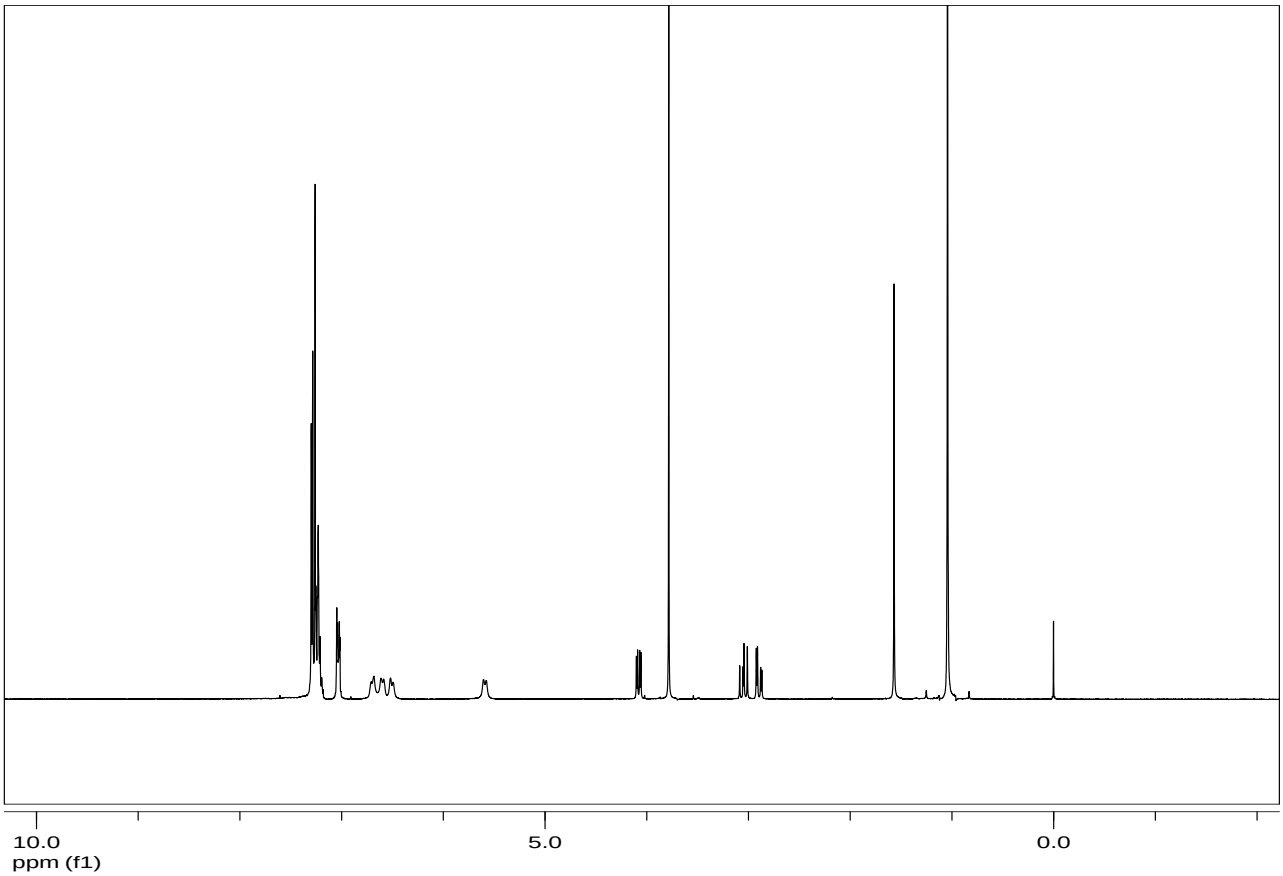


Fig. S12 ^{1}H NMR spectrum of compound **4** (300 MHz, $CDCl_3$)

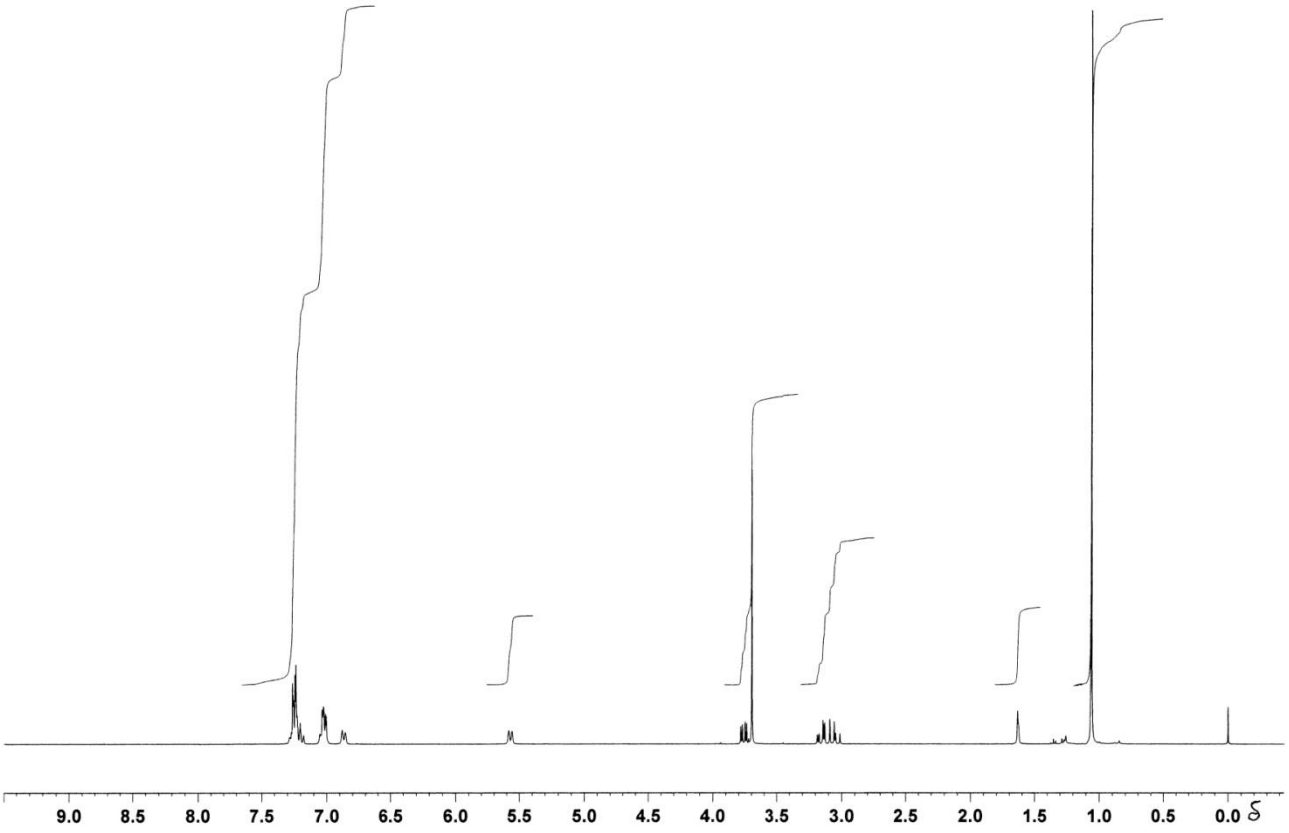


Fig. S13 ^{1}H NMR spectrum of compound **5** (300 MHz, $CDCl_3$)

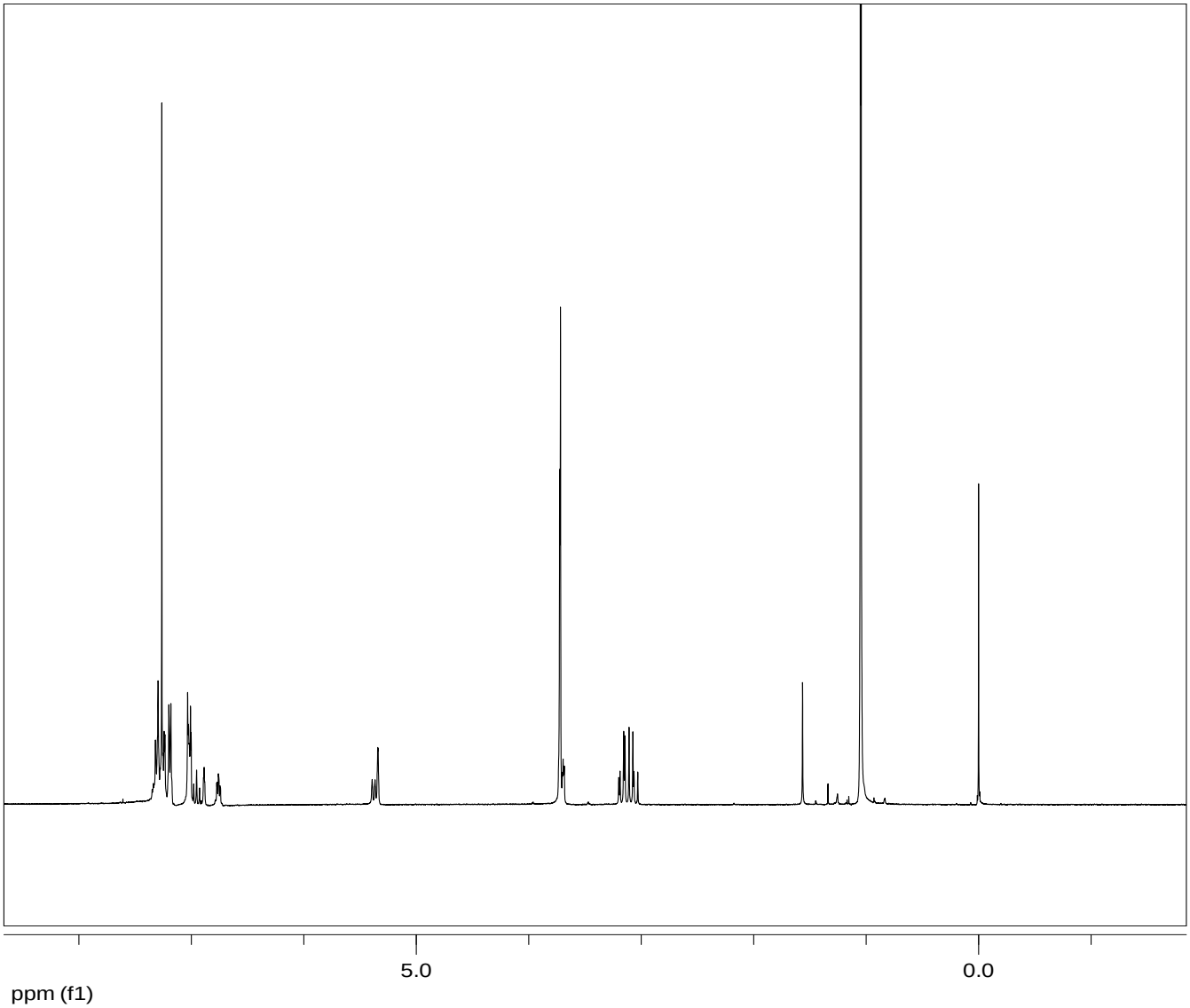


Fig. S14 ^{1}H NMR spectrum of compound **6** (300 MHz, $CDCl_3$)

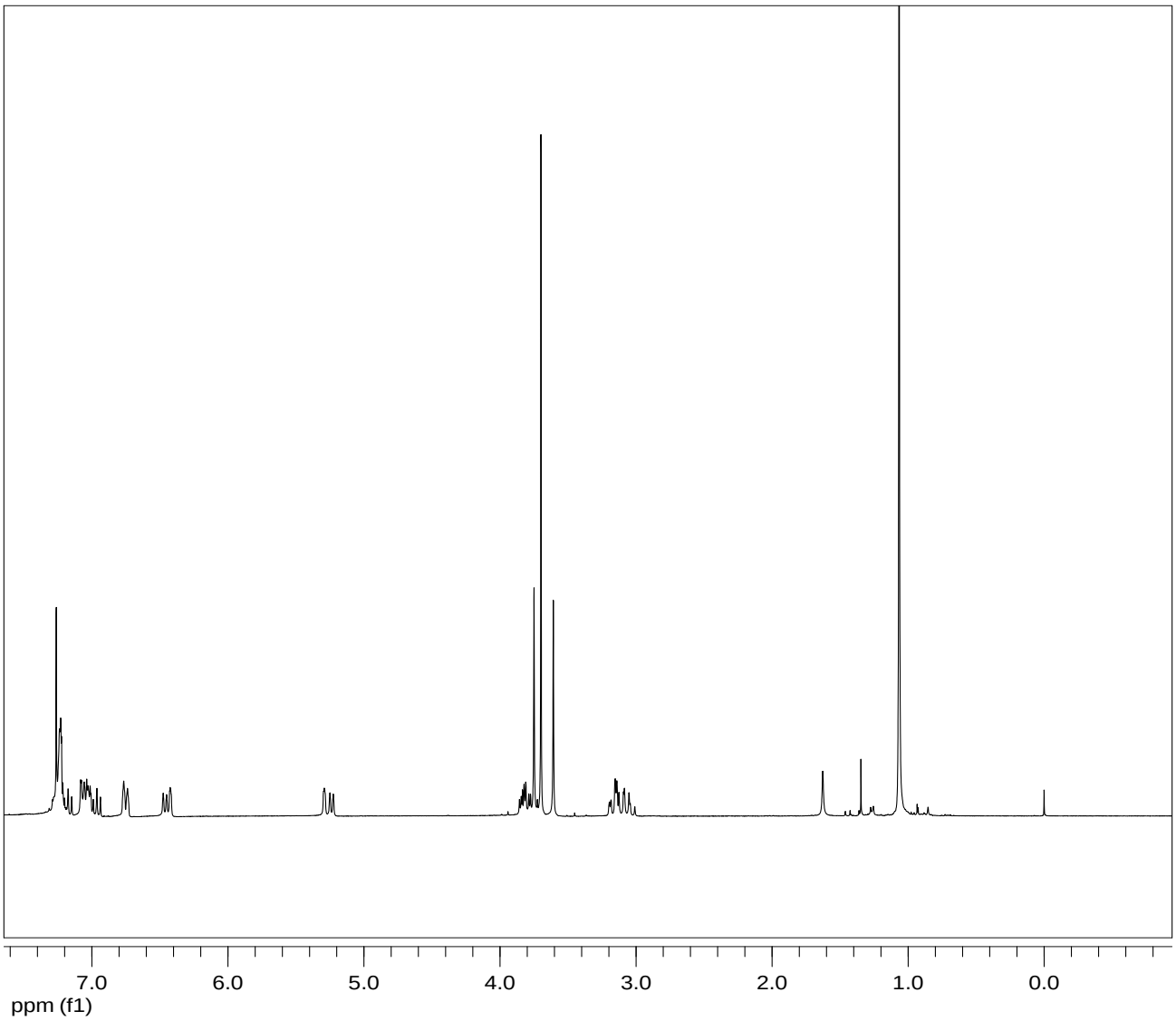


Fig. S15 ^{1}H NMR spectrum of compound **7** (300 MHz, $CDCl_3$)

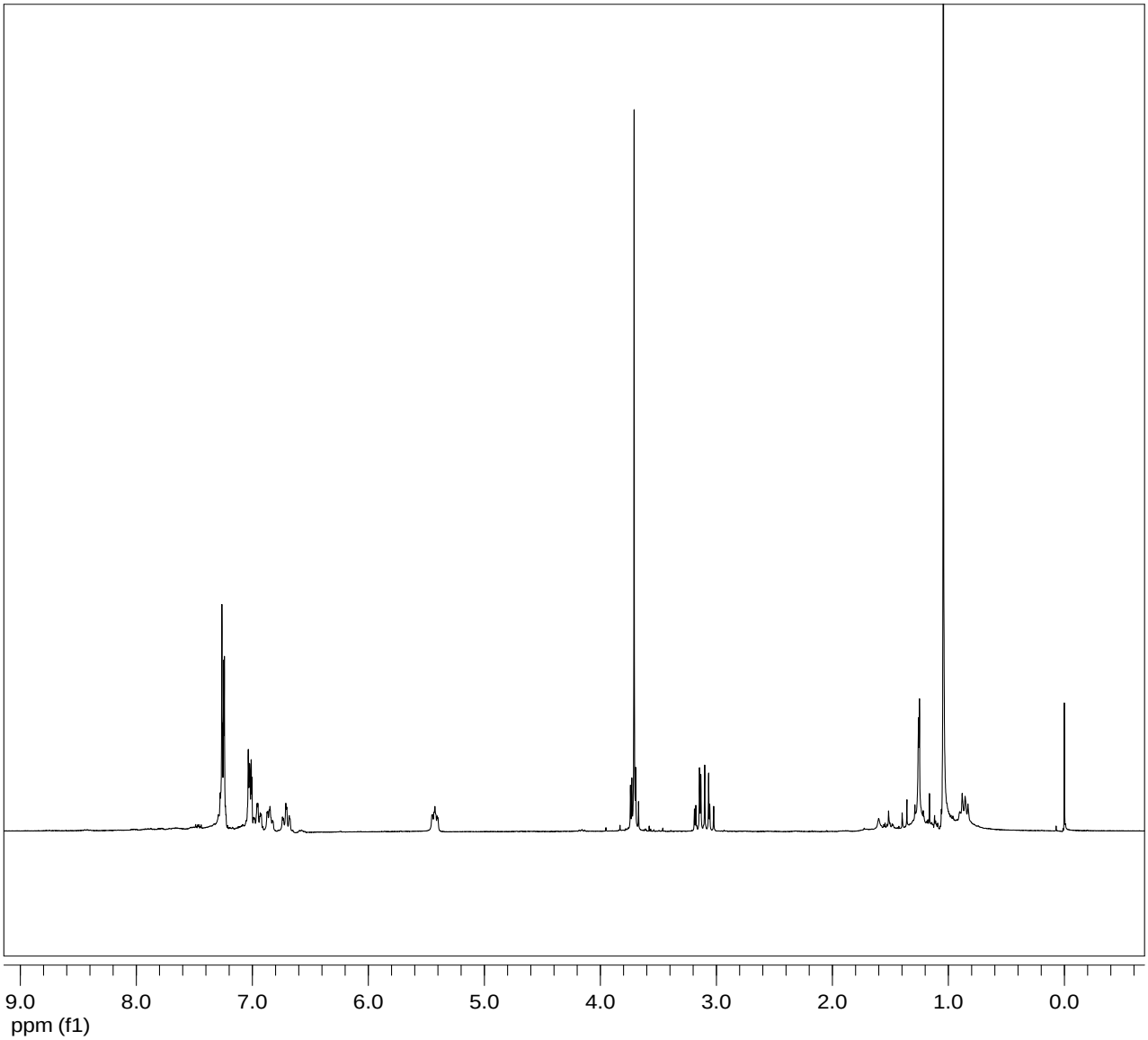


Fig. S16 ^{1}H NMR spectrum of compound **8** (300 MHz, $CDCl_3$)

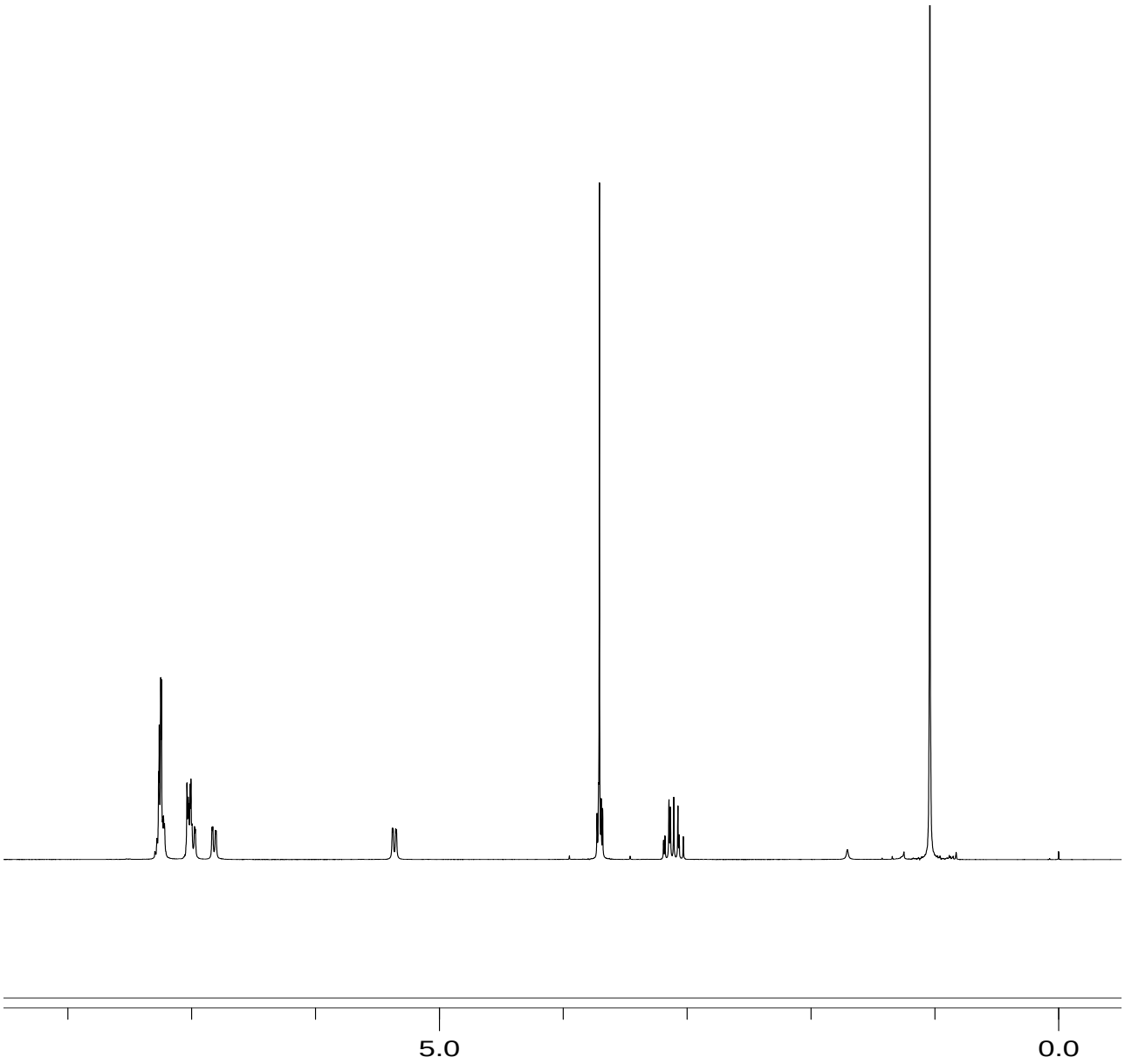


Fig. S17 ^{1}H NMR spectrum of compound **9** (300 MHz, $CDCl_3$)

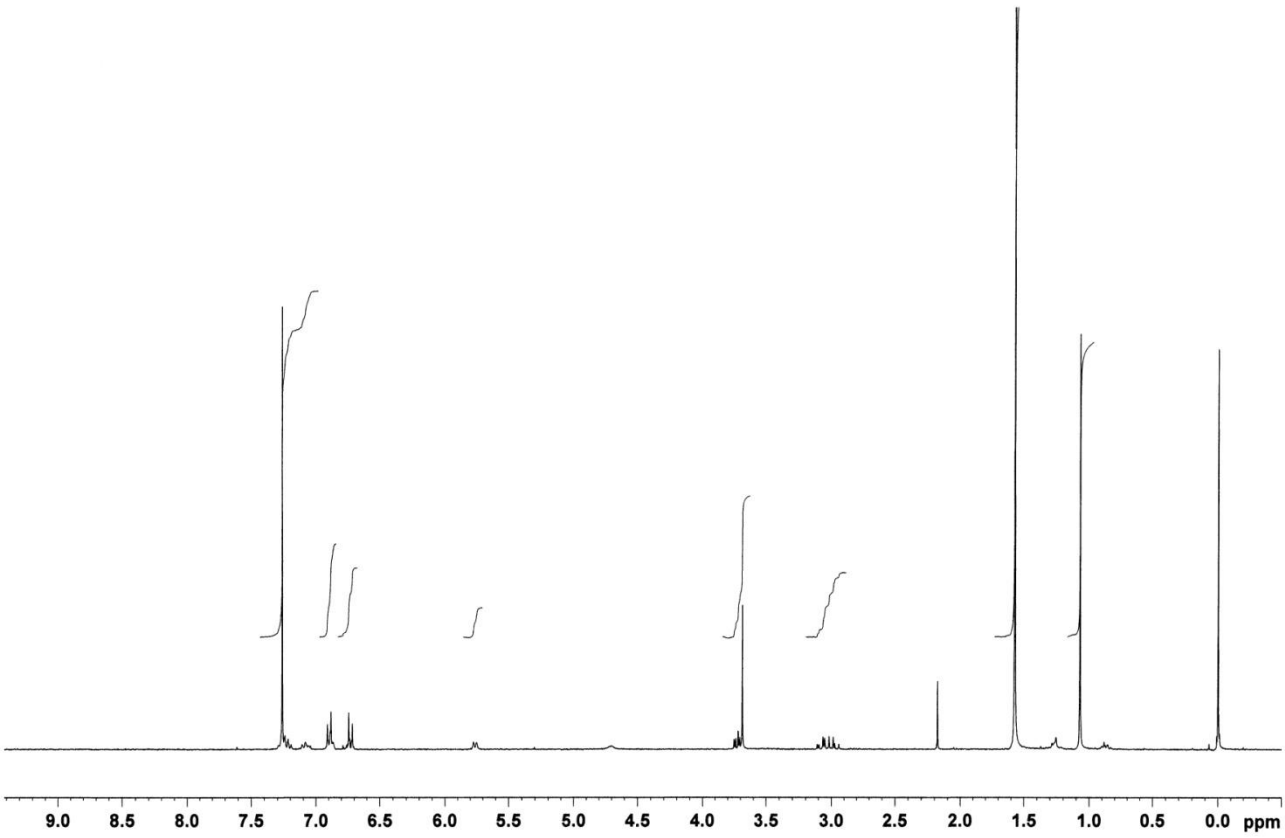


Fig. S18 ^{1}H NMR spectrum of compound **10** (300 MHz, $CDCl_3$)

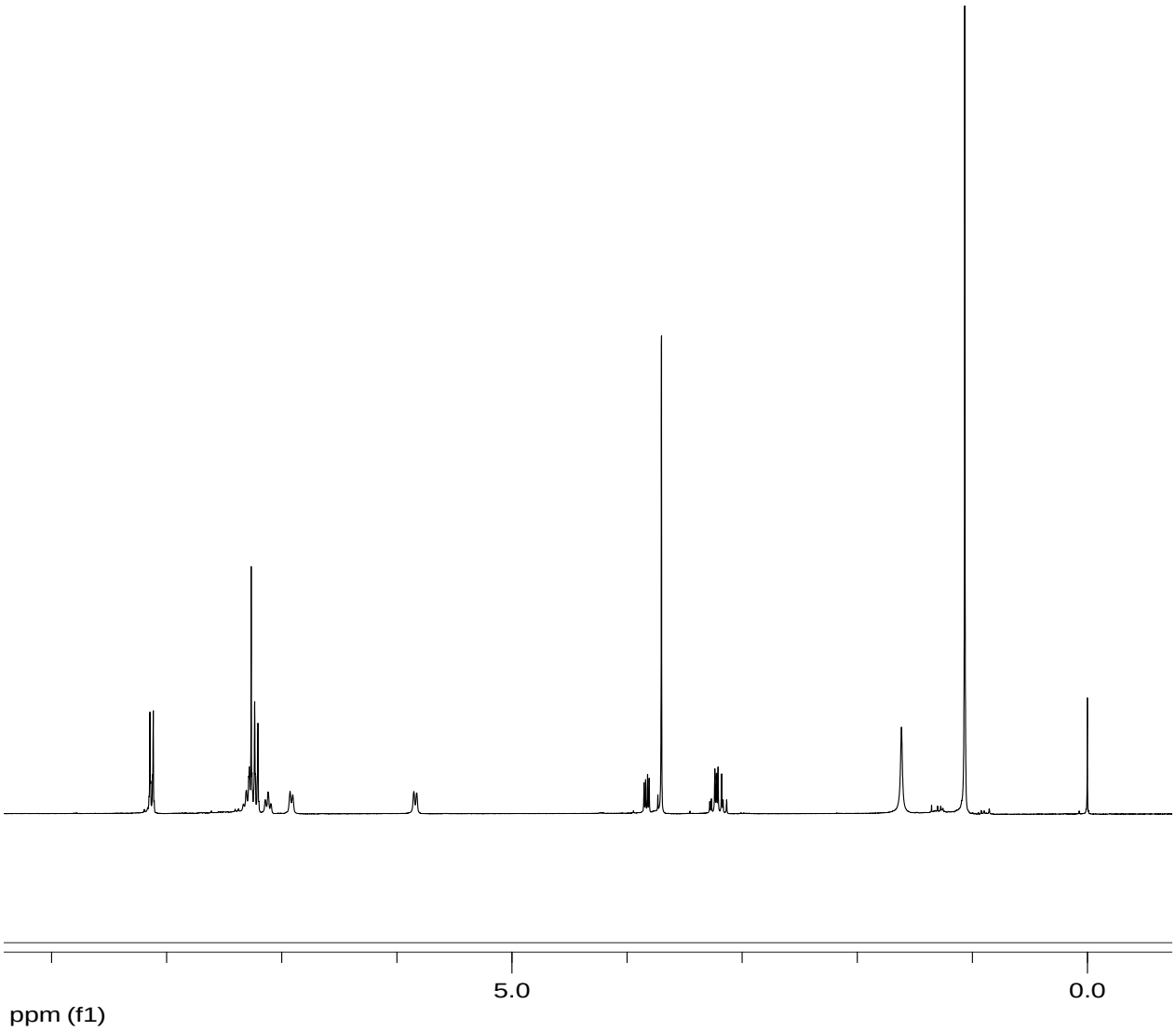


Fig. S19 ^{1}H NMR spectrum of compound **11** (300 MHz, $CDCl_3$)