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Supporting Information

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Gas Hosting in Enantiopure Self-Assembled Oximes

Alessandro Scarso,* Leonardo Pellizzaro, Ottorino De Lucchi, and Fabrizio Fabris*
Dipartimento di Chimica, Università Ca' Foscari di Venezia. Dorsoduro 2137, I-30123 Venezia, Italy.
Phone +39-41-2348908. Fax +39-41-2348517. E-mail: fabrisfa@unive.it
Anthony Linden
Institute of Organic Chemistry, University of Zurich. Winterthurerstrasse 190, CH-8057 Zurich, Switzerland.
Phone +41-44-635-4228. E-mail: alinden@oci.uzh.ch

(13 pages)

General. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 and 75.48 MHz respectively and the δ values in ppm are relative to TMS.

Materials. Reagents and solvents are all commercial products and were used without further purification. Triol **1** was prepared following a previously reported procedure.[1] Complete operating procedures as well as characterizations are reported in the Supporting Information.

Gas Binding Experiments. These were carried out by means of simple direct bubbling of the proper gas through a glass capillary in the NMR tube containing **3** dissolved in the deuterated solvent. For the dilution experiments the concentration of **3** was determined by integration of the methyne resonance of the host vs the residual $CHCl_3$ peak present in the deuterated chloroform (99.8%).

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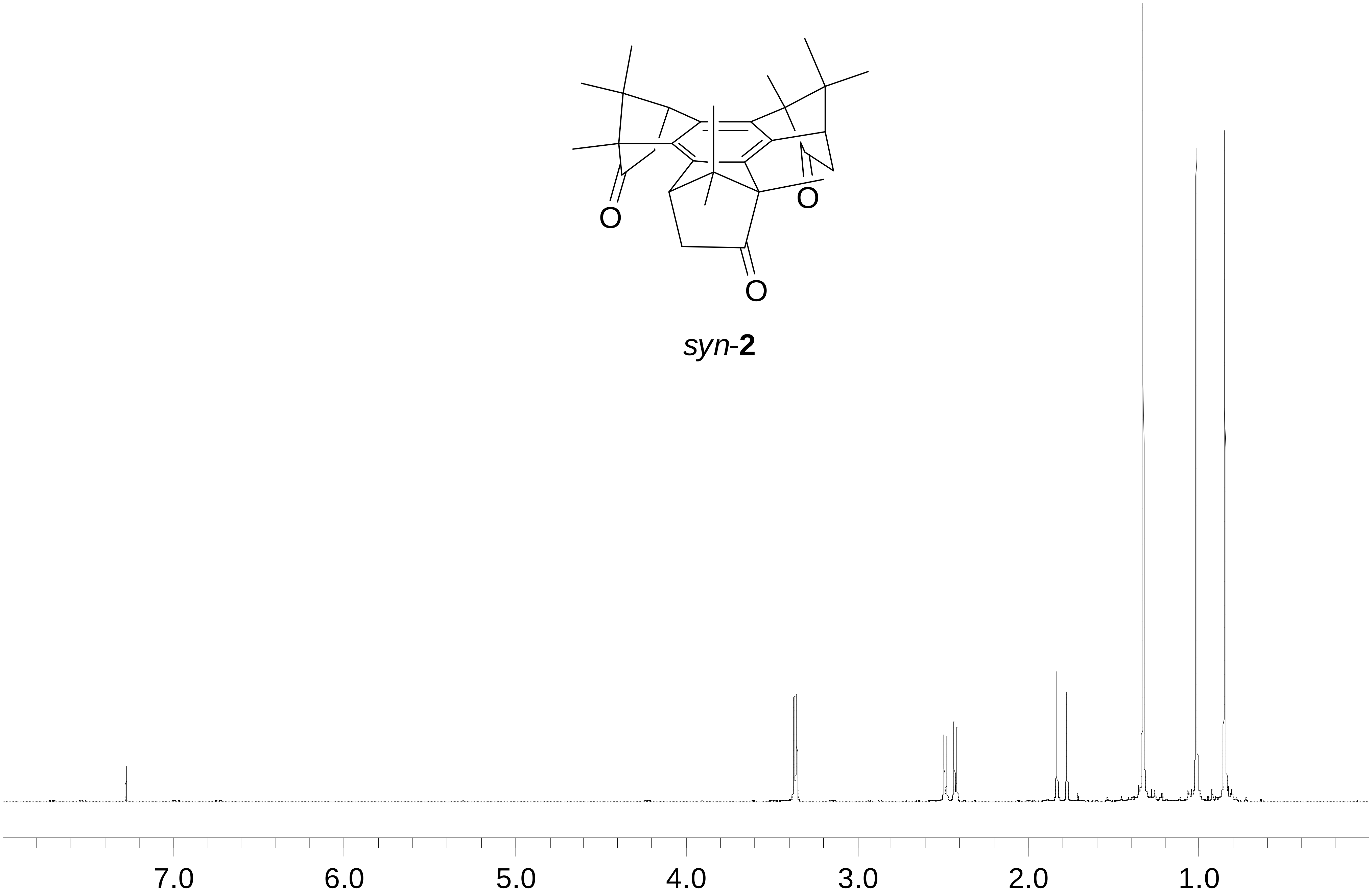
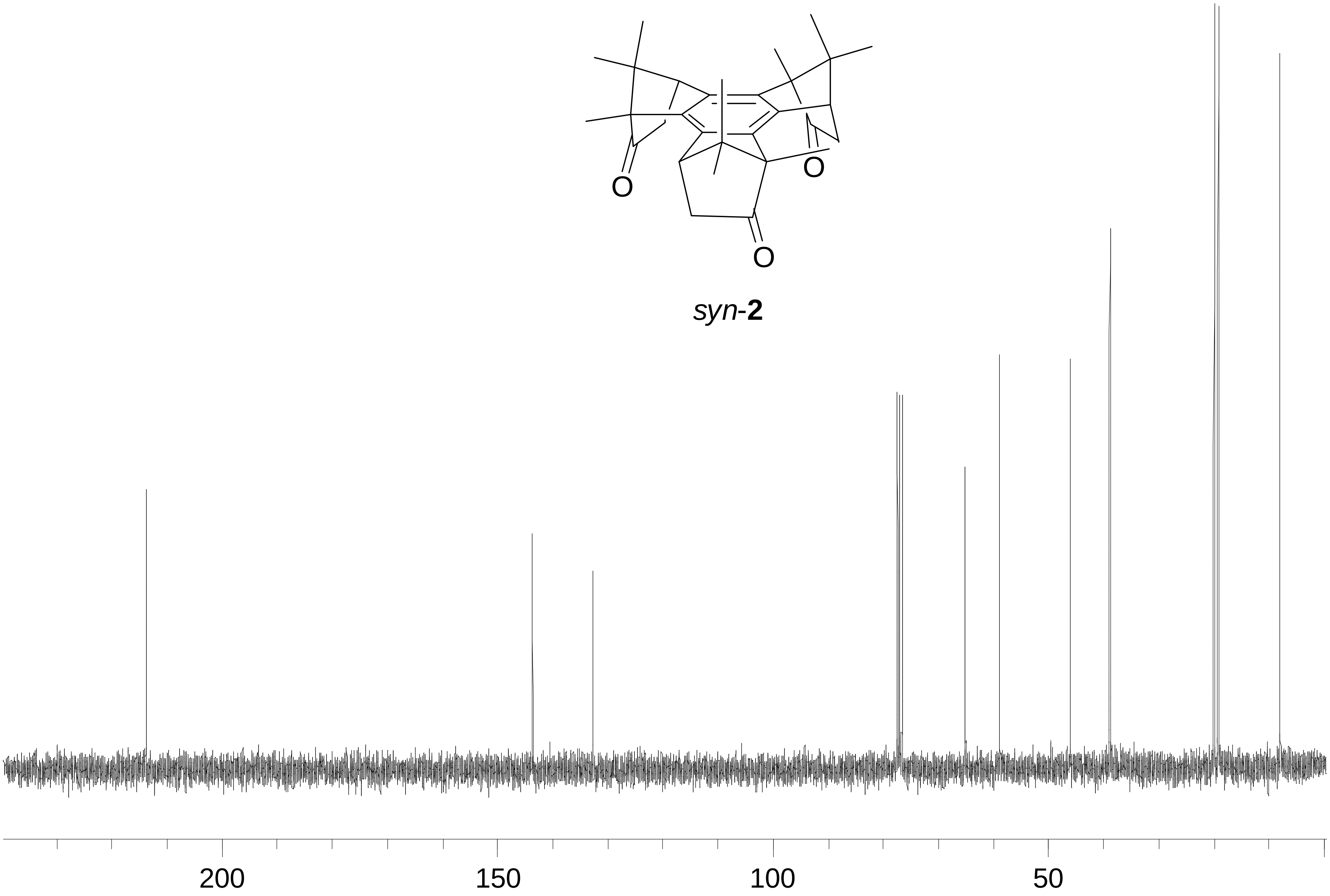
[1] a) F. Fabris, L. Bellotto, O. De Lucchi, *Tetrahedron Lett.* **2003**, *44*, 1211-1213; b) F. Fabris, L. Pellizzaro, C. Zonta, O. De Lucchi, *Eur. J. Org. Chem.* **2007**, 283-291.

Synthesis of (+)-*syn*-(1*R*,4*S*,5*R*,8*S*,9*R*,12*S*)-3,4,7,8,11,12-hexahydro-1,5,9,13,13',14,14',15,15'-nonamethyl-1,4:5,8:9,12-trimethanotriphenylen-2,6,10-trione (benzotricamphor **2**).

Oxalyl chloride 0.16 mL, 1.72 mmol) was added via syringe to a solution of dimethylsulphoxide 0.26 mL, 3.3 mmol) in dry dichloromethane (5 mL) at –60 °C. The solution was stirred at the same temperature for 5 min and a solution of *syn*-benzotriborneol **1** (100 mg, 0.22 mmol) in dry dichloromethane (2 mL) was added. After 30 min, triethylamine (3 mL) was added and the solution was allowed to warm to rt overnight. The resulting mixture was poured into satd. $NaHCO_3$, extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with satd. NaCl, dried over MgSO4 and concentrated at reduced pressure to afford a crude material that was recrystallised from hot MeOH to give 73 mg (75% yield) of colorless crystals, m.p. = 272-273 °C. $[a]_D^{22}$ = +691 (*c* 1.4, $CHCl_3$); IR (KBr) ? 2966(s), 1739(s), 1038(s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): d = 3.36 (d, *J* = 4.0 Hz, 3 H), 2.46 (dd, *J* = 17.6 and 4.0 Hz, 3 H), 1.80 (d, *J* = 17.6 Hz, 3 H), 1.33 (s, 9 H), 1.02 (s, 9 H), 0.85 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): d 213.8, 143.6, 132.6, 65.1, 58.8, 46.1, 38.9, 20.0, 19.2, 8.0; *m/z* (EI, 70 eV): 444 (M^+, 50), 402 (100), 374 (58), 360 (87), 346 (68), 331 (79%).Elemental analysis calcd (%) for $C_{30}H_{36}O_3$: C 81.04, H 8.16, found: C 81.00, H 8.18%.



syn-**2**



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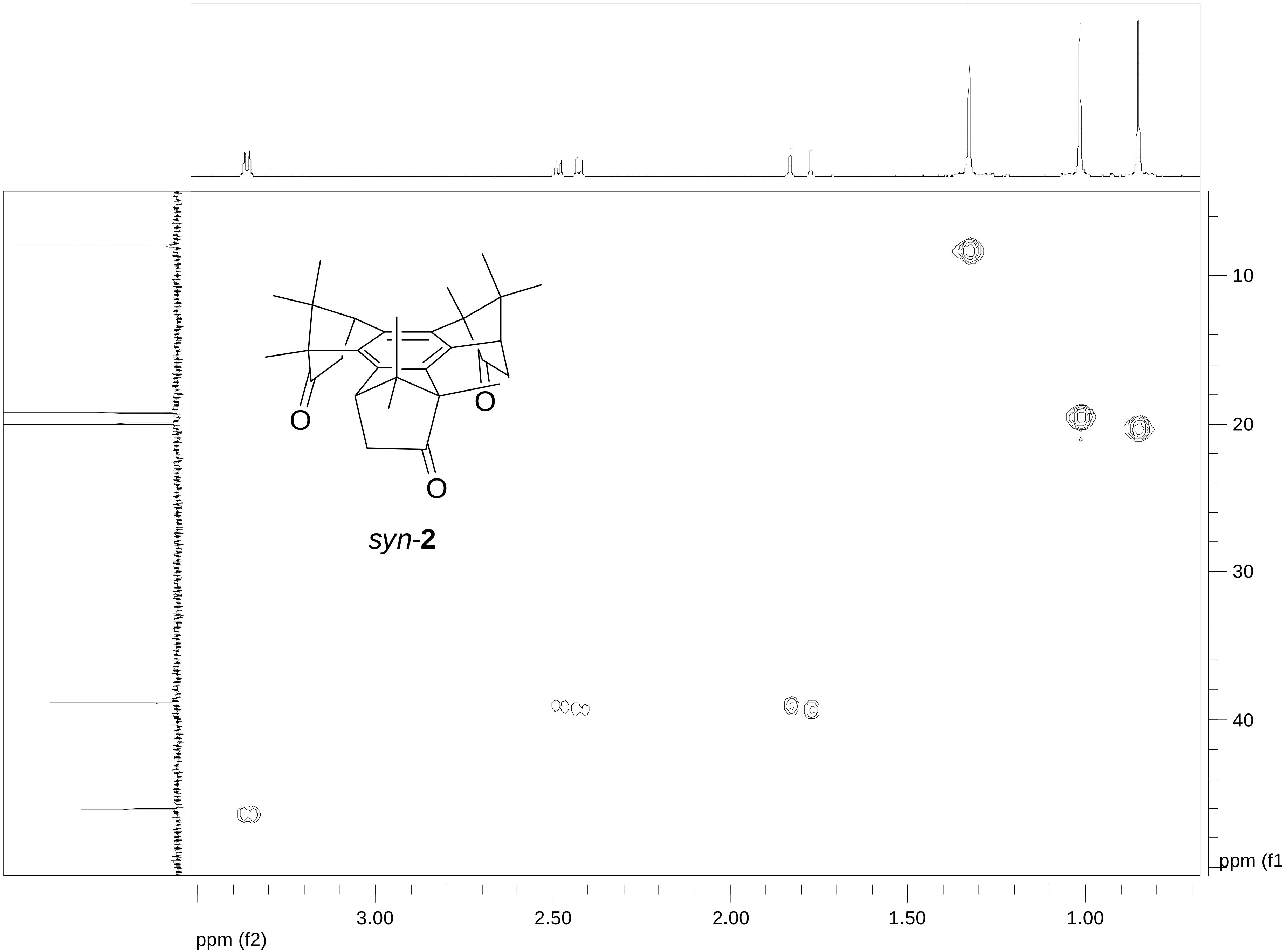
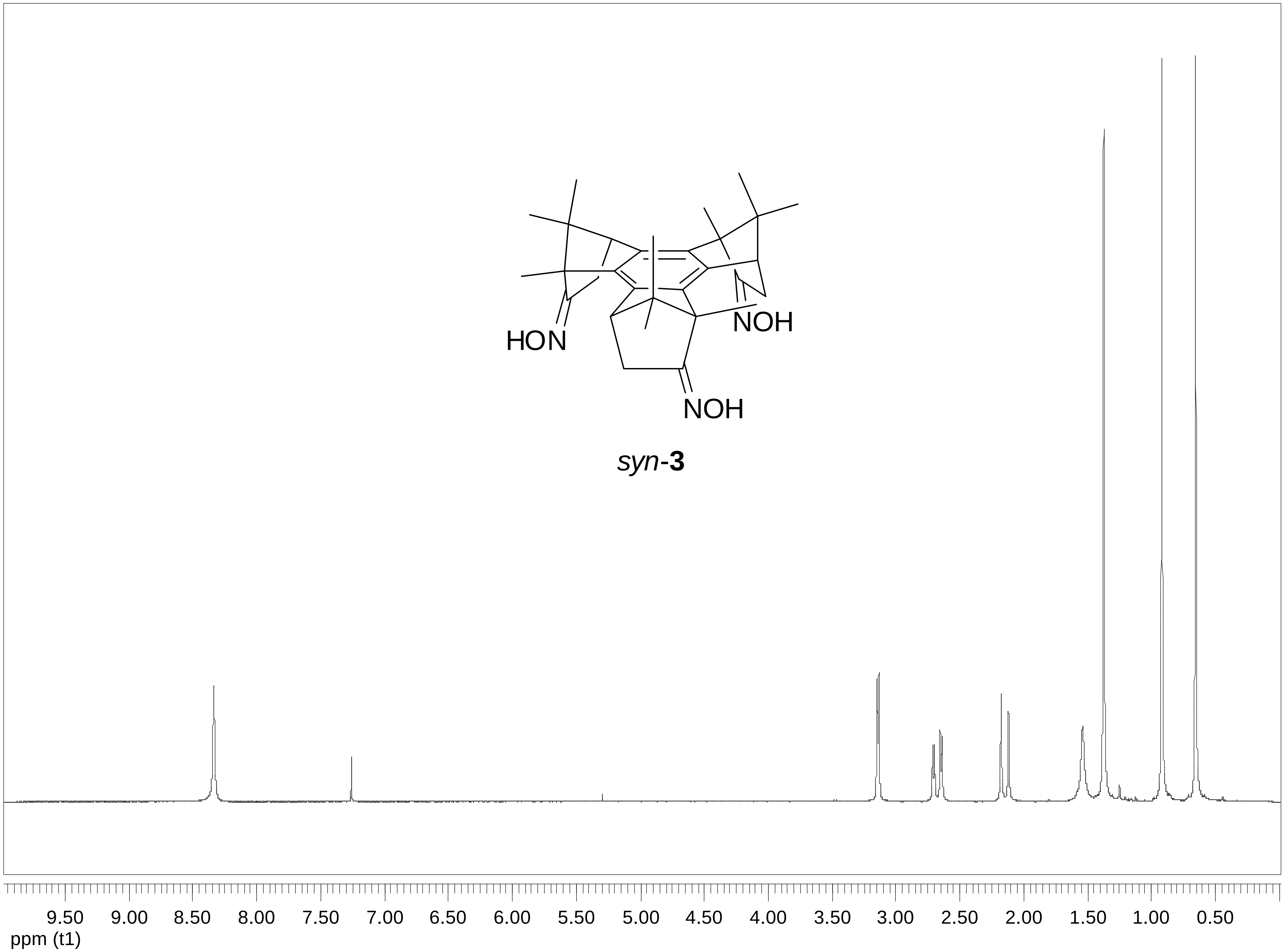
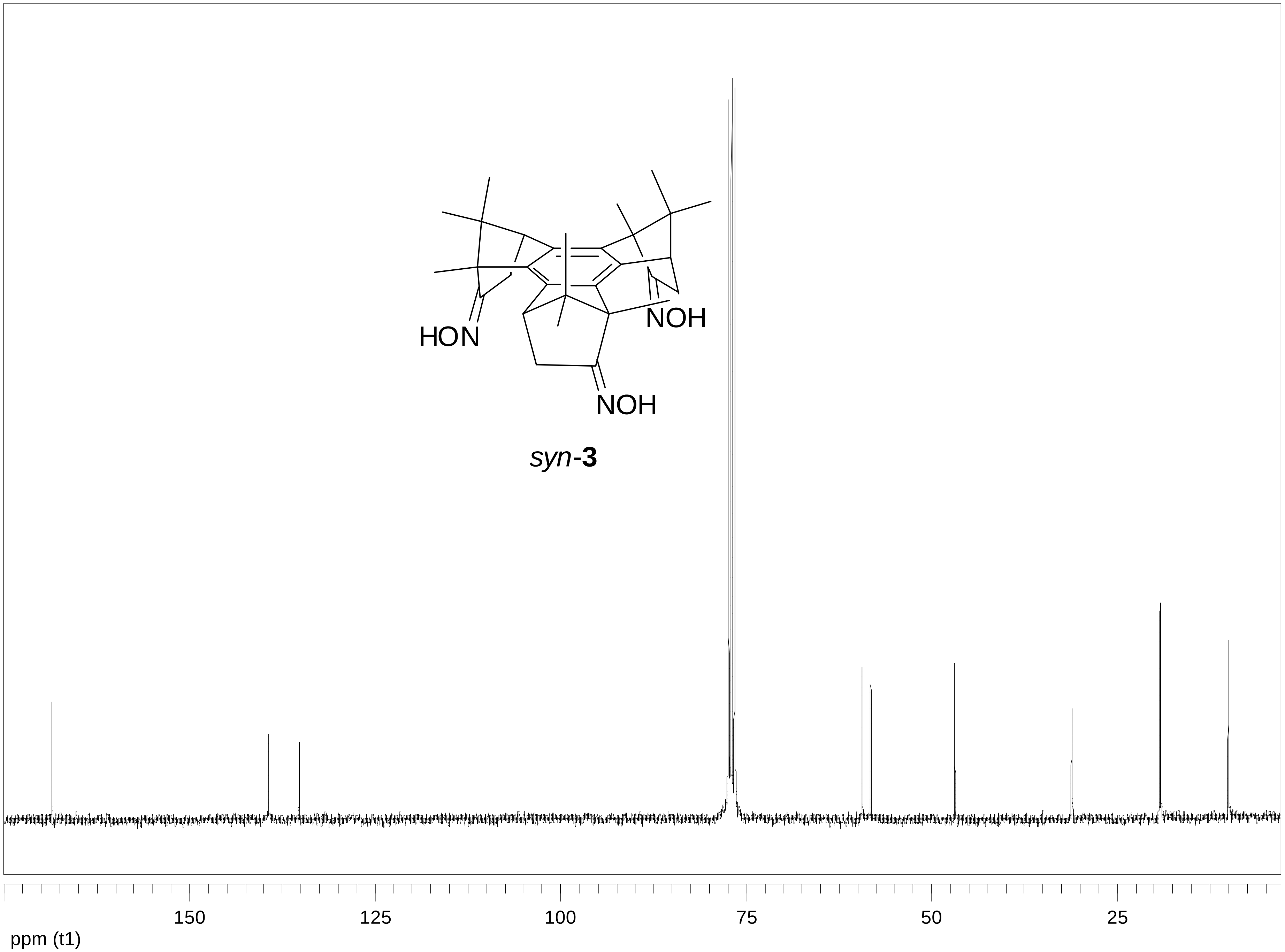


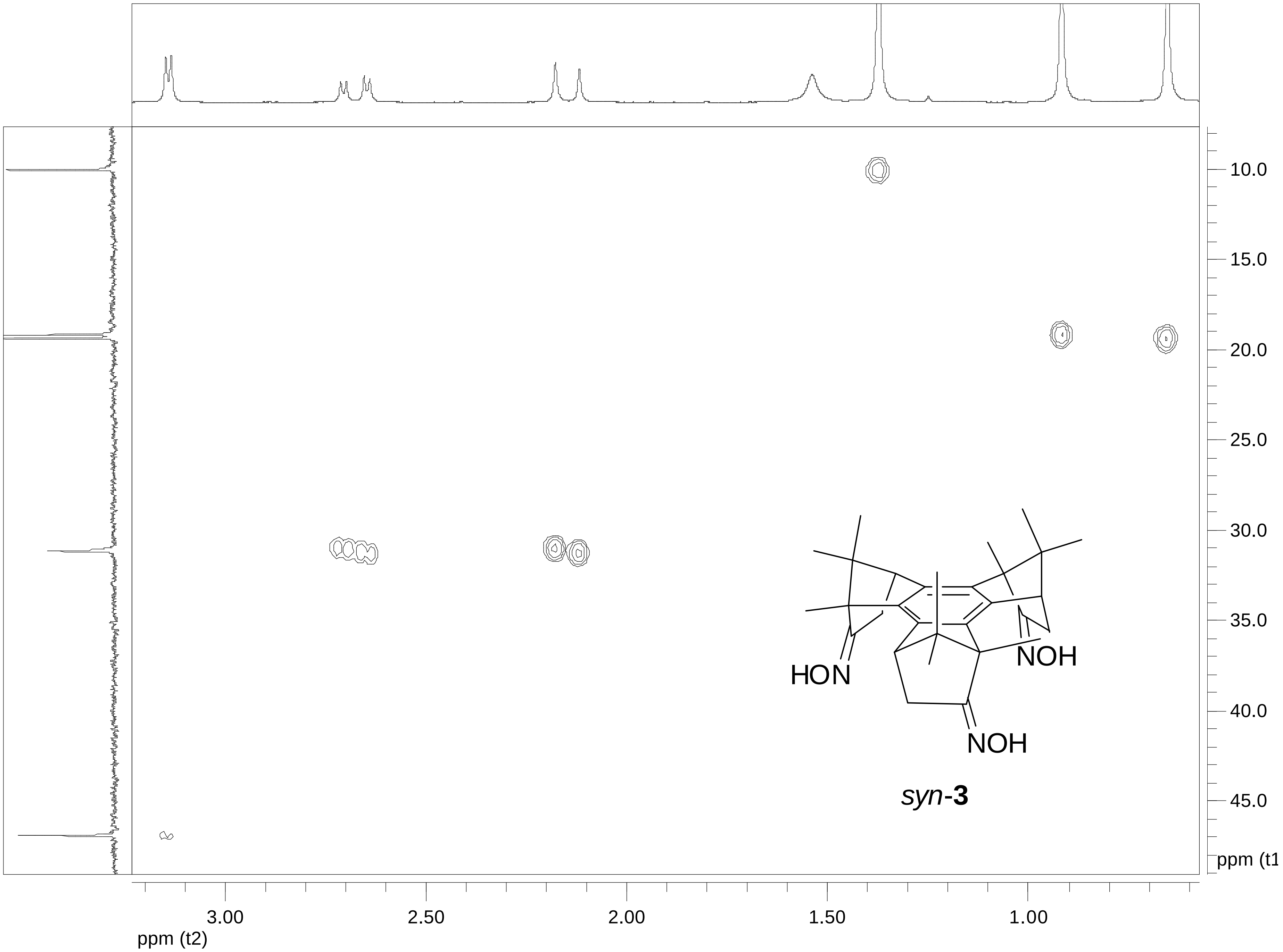
syn-**2**

Synthesis of (+)-*syn*-(1*R*,4*S*,5*R*,8*S*,9*R*,12*S*)-3,4,7,8,11,12-hexahydro-1,5,9,13,13’,14,14’,15,15’-nonamethyl-1,4:5,8:9,12-trimethanotriphenylen-2,6,10-trioxime (benzotricamphor oxime **3**).

Sodium hydroxide (390 mg, 9.75mmol) was added to a slurry of *syn*-benzotricamphor **2** (120 mg, 0.27 mmol) and hydroxylamine hydrochloride (330 mg, 4.68 mmol) in a 1:1 mixture of ethanol/water (4 mL). The resulting solution was sealed and stirred at r.t. for 72 h. The resulting crude was concentrated at reduced pressure, diluted with water and filtered. The residue was washed with cold water, dried with a stream of air and washed with dichloromethane to afford an off-white solid that was dried in vacuum over P_2O_5 (85 mg). Concentration of dichloromethane washings afforded unreacted benzotricamphor **3** (40 mg, conversion 65%). Yield of converted material 98%. m.p. = 274-276 °C (dec.); $[a]_D^{22}$ = +206 (*c* 0.8, MeOH); IR (KBr) ? 3356(s), 2970(s), 1676(w), 1637(w), 1446(m), 1388(s), 939(s), 906(m) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): d = 8.34 (br s, 3 H), 3.14 (d, *J* = 4.0 Hz, 3 H), 2.68 (dd, *J* = 17.6 and 4.2 Hz, 3 H), 2.15 (d, *J* = 17.6 Hz, 3 H), 1.37 (s, 9 H), 0.92 (s, 9 H), 0.66 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): d = 168. 6, 139.3, 135.2, 59.4, 58.2, 46.9, 31.1, 19.4, 19.2, 10.0. HRMS (ESI^+) *m/z:* calcd for $C_{30}H_{40}N_3O_3$: 490.3064; found: 490,3057.

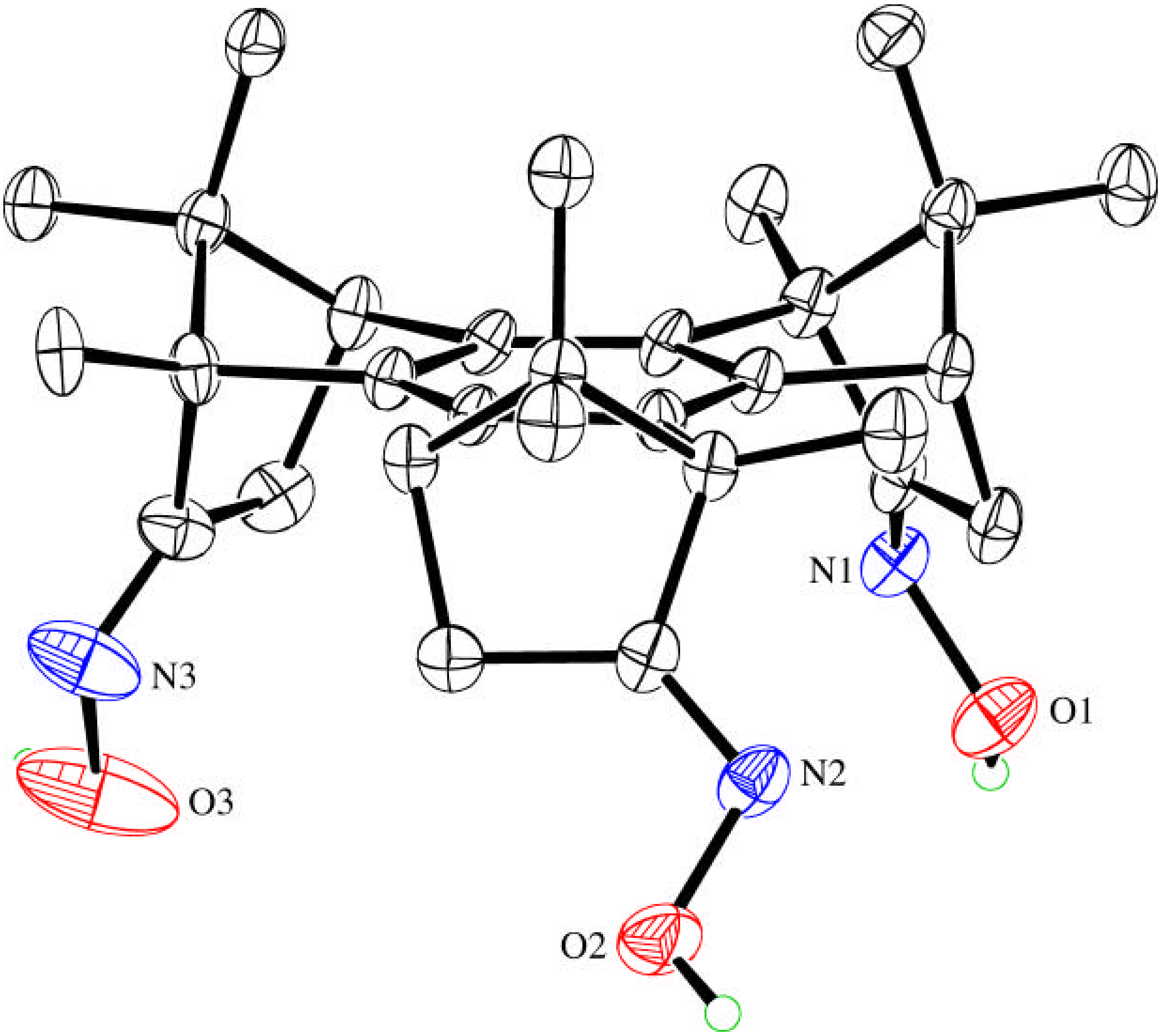

HON
NOH
NOH
syn-3
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)


HON
NOH
NOH
syn-**3**
150
125
100
75
50
25
ppm (t1)

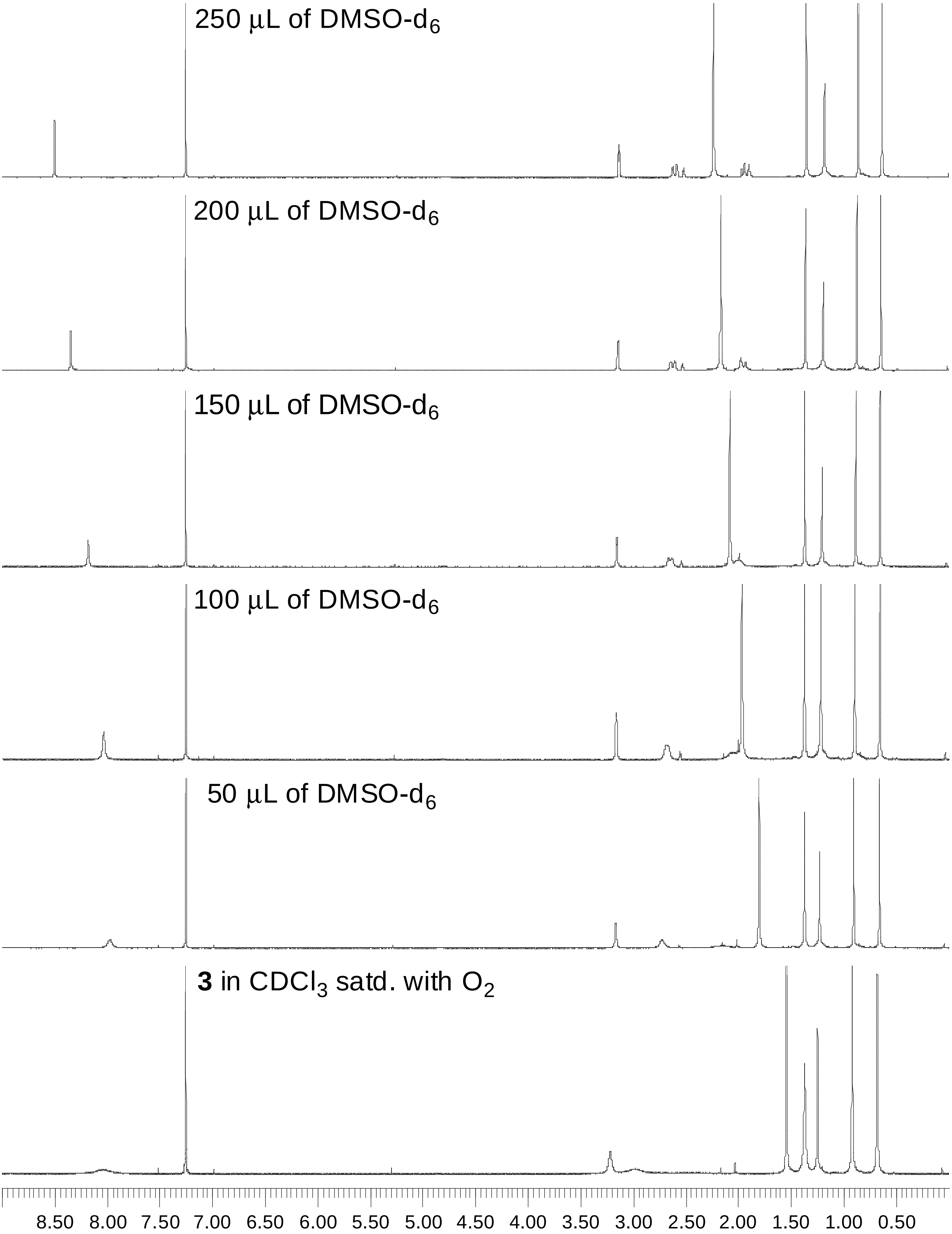

10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
ppm (t1
3.00
2.50
2.00
1.50
1.00
ppm (t2)
HON
NOH
NOH
syn-**3**

Crystallographic data

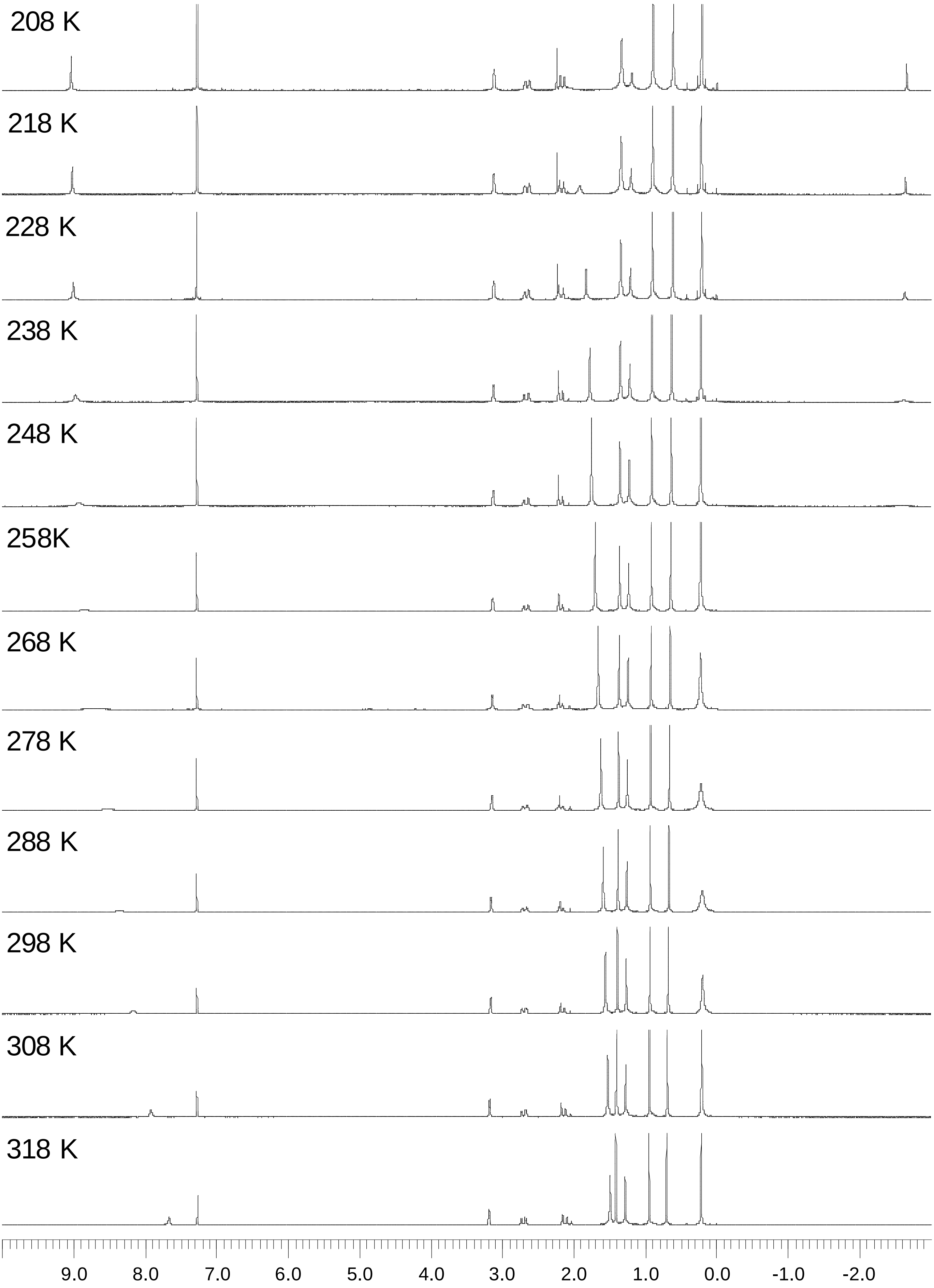
The molecular structure of **3** in the crystal structure of **3**?H_2O.



Needles suitable for an X-ray crystal-structure determination were obtained by slow evaporation of a solution of **3** in wet methanol.



^{1}H NMR spectra of an O_2 saturated $CDCl_3$ solution of **3** with increasing amounts of coordinating solvent dmso-d_6.



Temperature dependent ^{1}H NMR spectra of a CH_4 saturated $CDCl_3$ solution of **3**.

Determination of association constant

The association equilibrium constant for the supramolecular complex $N_2@\mathbf{3}_2$ was evaluated on the basis of the following equilibrium:

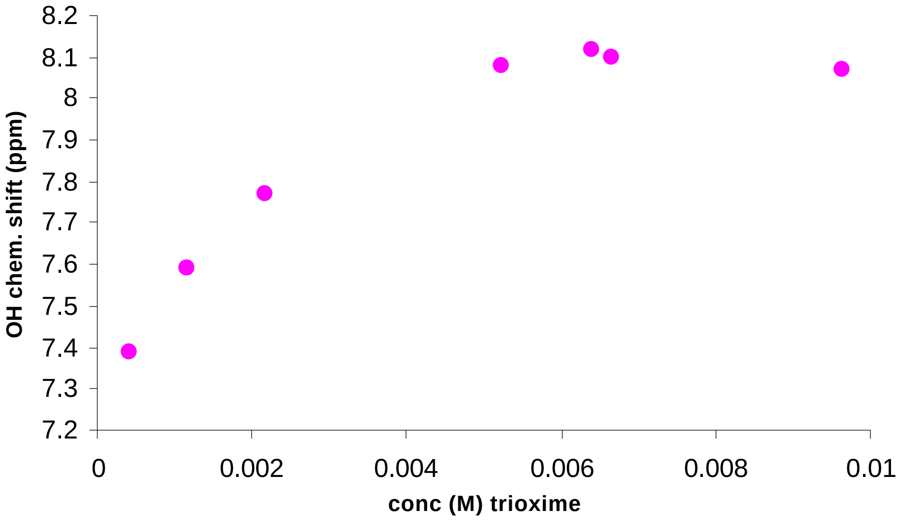
$$2\cdot\mathbf{3} + G = (\mathbf{3}\cdot G\cdot\mathbf{3})$$

$$K_{eq.} = [(\mathbf{3}\cdot G\cdot\mathbf{3})]/\{[\mathbf{3}]^2\cdot[G]\}$$

For the dilution experiments, the N-OH chemical shift is reported *vs.* **3** concentration determined by integration using as an internal standard the signal of the residual $CHCl_3$ present in the deuterated solvent $CDCl_3$. The N_2 solubility in chloroform was calculated to be about 50-100 mM on the basis of data reported in the literature.[i] The value is about one order of magnitude larger than the maximum concentration of **3** employed. Therefore, in the equilibrium, constant [G] can be assumed constant and interpolation of dilution data allowed the extrapolation of the [**3**] when the chemical shift is $\Delta\delta/2$. For that particular value of $[\mathbf{3}]_{(\Delta\delta/2)}$, the equilibrium constant simplified is:

$$K_{eq.} = 1/\{[\mathbf{3}]_{(\Delta\delta/2)}\cdot[G]_0\}$$

And the value calculated is $\sim 1\cdot 10^4\ M^{-2}$.



Plot of oxime N-OH chemical shift *vs.* Trioxime **3** concentration in $CDCl_3$.

References

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[i] Gas solubility in organic solvents: E. Wilheim, R. Battino, *Chem. Rev.* **1973**, *73*, 1-9.